ABSTRACT

Title of Document: THE EFFECTS OF DRAINAGE DITCH FILTER COMPOSITION ON HYDRAULIC PROPERTIES AND P SORPTION

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Phosphorus (P) in agricultural runoff is considered a primary contributor to waterway eutrophication. Currently filters made with P-sorbing materials (PSMs) in drainage ditches have been shown to effectively remove P in some situations, but further optimization is necessary. Sorption isotherms were used to determine PSM and temperature effects on P sorption. No effect was found due to temperature, although significant differences were found among the materials used. The different mechanisms of P sorption suggest the retention time used was not suitable for this study. A mesocosm experiment was set up to maximize the flow through filters by mixing gypsum with sand to increase the hydraulic conductivity without sacrificing P sorption. The mixture containing 90% mined gypsum and 10% sand had the highest hydraulic conductivity without a reduction in total P sorption. The mixture containing 80% mined gypsum and 20% sand could have potential as an alternate mixture.

THE EFFECTS OF DRAINAGE DITCH FILTER COMPOSITION ON HYDRAULIC PROPERTIES AND P SORPTION

By

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Dedication

To Kotik, Gilly, Oliver, Piggle, and Eliza, for all their love and support.

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Chapter 1 - A Review of the Literature Pertaining to the Subject

Abstract

The over-application of phosphorus to agricultural fields over many decades has led to many soils in the Eastern United States nearing their P sorption capacity. This situation has resulted in a two-fold problem: soils are far less able to further adsorb excess phosphorus, and they are more likely to release phosphorus into groundwater (Kao and Blanchar, 1973; Sims, 1998). This situation has also accelerated eutrophication, which is a major problem in our waterways that leads to decreased water quality as well as imperils aquatic life. Many agricultural fields are artificially drained through drainage ditches, which are the convergence of overland flow as well as some groundwater flow and represent an opportunity to try to sorb as much phosphorus as possible before it enters the waterways.

Work is underway to identify materials that will serve to sorb phosphorus in a fiscally and environmentally sound manner. Many different application methods of these materials are being tested, with researchers looking for a combination of low cost, low contamination, and efficient P sorption. There are several confounding factors, such as differences in P speciation, differences in the amount of P already in the soil, and differences in preferential flow paths. Temperature is another possible confounding factor, as kinetic reactions tend to vary with temperature.

Phosphorus

In the latter half of the twentieth century, there was enough concern over water quality in the United States to pass sweeping legislation like the 1972 Clean Water Act, aimed at reversing the trend of poor quality in American surface waters. However, change has been slower than

expected. The United States Environmental Protection agency estimated in 2004 that 64% of lake acreage, 44% of stream length, and 30% of bay and estuarine area in the US are unsuitable for swimming or fishing (USEPA, 2004).

Agriculture is the largest source of water quality impairment for rivers and lakes in the US, and the third-largest source of pollutants to estuaries in the US (Parry, 1998). Most of the agricultural component of water quality impairment is due to fertilizer runoff and leaching into waterways. A commonly-used fertilizer is manure (and other organic wastes such as biosolids), as application of animal waste to nearby agricultural fields is less expensive than the transport of wastes away from the waste-producing facility, as well as being less expensive than chemical fertilizers. Application of manure fertilizer at N-based rates tends to apply 200-300% of phosphorus required for crop health (Parry, 1998). This over-application of phosphorus leads to the buildup of phosphorus in the soil, which was thought unimportant for many years, as phosphorus buildup does not have detrimental effects on fertility (Peterson et al, 1994). However, P buildup can lead to leaching of phosphorus through the soil profile (Kao and Blanchar, 1973). There is also a measurable amount of P desorption from fertilizer-amended soils which, while variable, tends to vary inversely with exchangeable calcium in the soils (Siddique and Robinson, 2004). It has also been found that heavily manured soils in contact with water have a P release rate ten times the critical environmental threshold for flowing waters and up to 30 times the P release rate of untreated soils (Dou et al, 2009).

Currently, fertilizer application rates are regulated based on amounts of nitrogen and trace elements. If limitations of application were to be imposed based on phosphorus, manure application would become impossible in many areas due to already high P test levels (Penn and Sims, 2002). Also, in some simulated rainfall studies the amount of P applied in fertilizer has

been found to be one of the best indicators of P levels found in surface runoff immediately after application (Delaune et al, 2004). Unsurprisingly, P levels in runoff have also been found to be higher in fields that experience more soil erosion. However, there is some degree of complexity in terms of predicting total phosphorus loss from fertilizers. Reddy et al (1980) suggested the ratio between carbon and phosphorus in organic materials can be used as a predictor of whether those materials will increase or decrease phosphorus sorption, with a carbon/phosphorus ratio less than 130 indicating increased P desorption. However, this simple rule does not take into account the possibility of other materials that can increase phosphorus sorption, such as calcium or iron. Elliott et al (2005) found in a rainfall simulation study that with the fertilizers they were using, the fertilizer's phosphorus content was not a good predictor of dissolved phosphorus in runoff, especially in the case of the various biosolids used, as biosolids have numerous sources and can be processed in a number of ways before making it to the field as fertilizer. Many biosolids have significant amounts of iron, aluminum, and especially calcium in them, which can alter their P release characteristics (Penn and Sims, 2002).

Regardless of the fertilizer used, decreases in the remaining phosphorus sorption capacity with excess P applications increases the likelihood of P loss to surface waters via erosion and runoff (Mozaffari and Sims, 1996; Sims, 1998). This finding has been further elucidated by field studies that measured the phosphorus levels of surface runoff (He et al, 2006). These studies found P levels were higher in the case of fields that had more annual fertilizer applied, resulting in soils near their sorption capacity. One study found such fields to be at 80-90% of their potential P saturation, while unmanured soils were in the 11-33% range of P saturation (Dou et al, 2009). If soils have not been continuously fertilized at high rates of P, all but the sandiest soils have the P sorption capacity to prevent P leaching from a single application of fertilizer

(Elliott et al, 2002a). In contrast to these soils, fields that have reached their sorption capacity can leach phosphorus even several decades after the last P application (Djodjic et al, 2004; Nelson et al, 2005). Hooda et al (2000) found that total P sorption capacity is not an indicator of P release from soils, but rather the degree of P saturation predicts the amount of P leaching from those soils. Vadas et al (2005) reiterated this finding in a review of many studies that collectively showed that the degree of soil saturation is the best possible predictor of P in runoff.

Eutrophication

Eutrophication is the result of excessive growth of autotrophs such as cyanobacteria and algae due to high concentrations of nutrients in waterways. This high productivity leads to increased bacterial activity and respiration, which in turn leads to hypoxia or anoxia. Phosphorus (P) has been shown to be the principal limiting agent for the growth of autotrophs in fresh water, while nitrogen is the limiting agent in estuaries and marine environments (Correll, 1998). Because autotrophic uptake of phosphorus is one of the major concerns when discussing eutrophication of surface waters, it is common for different pools of phosphorus to be described so as to get an idea of the effects that phosphorus may have on eutrophication. Total phosphorus, dissolved reactive phosphorus, soluble phosphorus, particulate phosphorus, bioavailable phosphorus, and bioavailable particulate phosphorus are common measurements of P in leachate samples (McDowell and Sharpley, 2002). Soluble phosphorus is readily available to aquatic autotrophs and can be used as a measure of available phosphorus, but, for example, P bound by Ca and Mg is released under low pH conditions and can also be bioavailable under certain conditions (Leader et al, 2008).

Therefore, the environmental regulations of most states recognize that loosely bound particulate P is also an important factor, so the particulate P fraction of total P is also taken into

account when sites are assessed for P management (Ippolito et al, 2007). White et al (2009) confirmed on a field scale numerous studies that showed that an understanding of the speciation of the phosphorus applied to the fields is critical to developing a good model for estimating bioavailable phosphorus in runoff. This result is especially true if the P source being considered is variable in terms of that speciation.

Because eutrophication is a primary concern when discussing phosphorus, a model describing phosphorus transport from the surface must include a number of factors salient to eutrophication: sources of P, amount of P and percentage of the total that is mobile, transport mechanism and the pathways P takes to waterways (Zaimes and Schultz, 2002). The first three factors are controlled by fertilizer applications or other amendments added to the soil, and the last two factors vary by soil and by site.

Chesapeake Bay Area

The Chesapeake Bay is the largest estuary in the United States whose watershed incorporates parts of six states and the District of Columbia with a population of 15 million people. The health of the bay has been in decline, and for much of the 20th century efforts have been ongoing to try to restore the ecosystem. Because it is such a large and important estuary, the Chesapeake has become a model for aquatic ecosystem restoration (Boesch et al, 2001).

In the year 2002, 408 surface waters in Maryland were identified as "impaired," meaning they were not fully capable of satisfying their designated uses as recreational waters, drinking water sources, or other uses (USEPA, 2004). Twenty-five percent of those impairments were due to eutrophication. In recent years, the threat of eutrophication has been increasingly recognized, leading to best management practices being instituted in the Chesapeake Bay watershed with the objective of reducing phosphorus loads entering the bay.

Ditches

There are two perspectives of the effect drainage has on P transport. The first perspective is that the drainage provides a route of preferential flow for phosphorus, bypassing most of the soil and its possible retention abilities. The second perspective is that by reducing the amount of waterlogged soil, more P can be retained through redox processes (Kroger et al, 2008). There is evidence for both perspectives in the literature, as artificial drainage has sometimes resulted in reduced P going into waterways, and other times when there has been no effect or even increased P entering waterways (Sims et al, 1998). Whether drainage has positive or negative effects on soil P retention, drainage represents the convergence of surface runoff and groundwater leaving agricultural fields. Drainage ditches are also a direct link to natural waterways, and thus can be considered a point source of P entering waterways.

In terms of drainage ditches' contribution to eutrophication, Dodds et al (1998) suggested an eutrophication threshold of 0.02 mg P/L for flowing waters of low velocity was a concern for its contribution to eutrophication. A subsequent study of the Coastal Plain of Maryland found that every drainage ditch in the study area exceeded the threshold proposed by Dodds et al (Kleinman et al, 2007).

It has been found that the P distribution within drainage ditches can vary, with higher P concentrations found in the surficial soil closest to point and nonpoint sources of P, and also where soil evolution has released significant amounts of iron oxides (Vaughan et al, 2007). Iron oxides are exceptional binders of P to their surfaces, so their presence within ditches greatly increases sorption. This sorption and the natural activity of the soil mean that ditches are not only the conduit by which P enters waterways, but also provide an opportunity to capture P before it enters aquatic systems.

Kroger et al (2008) found that agricultural drainage ditches in the Mississippi River basin had the potential to reduce inorganic P loss during storm events, and suggested ways to increase that reduction in P loss. Their primary suggestion was the introduction of weirs and other flow control structures to increase retention time to allow for potentially increased P sorption.

Phosphorus Loss Due to Storm Events

As discussed before, ditch flow is a combination of surface runoff and groundwater flow. The base amount of ditch flow consists mainly of groundwater, whereas during storm events the vast majority of flow through the ditch consists of surface runoff (Ward and Trimble, 2003). Further, storm events contribute a vastly disproportionate amount of the P exported from the watershed given their relatively small contribution to total flow (Heathwaite and Dils 2000). This apparent discrepancy is because precipitation provides the major source of the energy required for phosphorus transport (Zaimes and Schultz, 2002).

Phosphorus Sorbing Materials

Phosphorus Sorbing Materials (PSM) are materials that remove soluble phosphorus from solution. They tend to contain iron (Fe), magnesium (Mg), calcium (Ca), and/or aluminum (Al), and operate by the combined processes of adsorption and precipitation (Penn et al, 2007). The single word "sorption" has been adopted by some to mean the removal processes ranging from adsorption to precipitation (McBride, 1994). The selection of which PSMs to use as a means of mitigating P loss depends on a number of factors, including: base cost, transport cost, speed of P sorption, P sorption as a ratio to tons PSM added, maximum potential to sorb P, toxicity, and potential use as a fertilizer after P sorption. Some examples of PSMs are water treatment residuals, steel slag, alum, and gypsum.

Water Treatment Residuals (WTR) contain amorphous Al and Fe salts, which were used in the water treatment process to remove turbidity and color (Elliott et al, 2002b). These salts makes residuals a useful sorbing material, as amorphous Al has been shown to be the form responsible for P retention, as opposed to total Al (Dayton and Basta, 2005). Field testing of WTRs has shown that they can have a P sorption rate ranging from 3500 to 5000 mg P/kg, which depends partially on the makeup of the WTRs used (with Al-based WTRs sorbing more P/kg than Fe-based) (Makris et al, 2004a). The theoretical maximum for WTRs exceeds 9100 mg P/kg, but the actual efficiency is less due to limited surface area availability (Makris et al, 2004b). Further, it was found that the presence of carbon in the WTRs tended to cause greater microporosity, but decrease the total sorption of P per unit surface area, further confounding our understanding of the P sorption model (Makris et al, 2005).

Alum ($Al_2(SO_4)_3 \cdot 14H2O$) is a commonly used amendment for P sorption that works by dissociation of Al^{3+} ions, which form a poorly crystalline solid resembling that found in WTR. The problem with using alum is its efficacy decreases with a decrease in pH, and alum itself is a highly acidic substance (liquid alum has a pH of 2.4). Even in systems with a very high buffering capacity, alum was outperformed in terms of P sorption capacity by WTR alternatives (Malecki-Brown and White, 2009). There is also some concern about the potential release of aluminum ions, as they can be toxic to plants and aquatic ecosystems. However, alum has been tested extensively as an additive to poultry litter in an attempt to decrease P solubility (Sims and Luka-McCafferty, 2002), and it has been shown to be effective in this role.

Bastin et al (1999) explored the use of a combination of iron oxides and gypsum in an attempt to capture as many forms of phosphorus as possible, and concluded gypsum has promise as a PSM that should be investigated further. Callahan et al (2002) performed an incubation

study that combined field soils with seven different PSMs: anthracite refuse ash, bituminous refuse ash, by-product gypsum, siderite, steel-processing sludge, WTRs, and wollastonite. These PSMs were mixed with the field soils at different rates representative of field application and incubated with periodic wetting. The researchers found the PSMs tested with the greatest potential for phosphorus sorption were bituminous refuse ash, WTR, and by-product gypsum.

The aquatic microbial mats that can grow in the boundary region between the oxic and anoxic zones in streams have also been identified as a PSM, as their metabolism depends on the production of biogenic iron oxides (Rentz et al, 2009). This biogenic PSM has been shown to be as effective at P sorption as other iron oxide-based PSMs, and has already been used in the water treatment industry. This PSM is different from many other PSMs in that there can be less chance of contaminants, and also there have been few PSMs identified that can be grown.

In the presence of organic fertilizers, the decomposition of organic materials tends to produce organic acids (Reddy et al, 1980), which can competitively exclude phosphorus from anion sorption sites both in the soil and on sorbing materials. Therefore it must be remembered in the evaluation of PSM that different fertilizers can have different effects on sorption beyond the total P applied.

Many of the candidate PSMs originated as municipal or industrial waste, and as such are often contaminated with heavy metals and other pollutants. Supplies of many of the industrial byproduct PSMs currently under investigation can be obtained that are of "exceptional" quality for low presence of trace heavy metals under current EPA guidelines (Penn et al, 2011). However, O'Connor et al (2005) warned that there currently exists very little regulation in terms of allowable contaminants that can be applied to agricultural fields, and care must be taken with the application of PSMs to minimize the introduction of harmful materials into the watershed.

Application of Phosphorus Sorbing Materials

Methods of implementing the use of PSMs for field application include: surface application to buffer zones to create strips that capture phosphorus from field runoff before it reaches the field, incorporation directly into high-P fields, mixing directly with soil amendments, and the creation of drainage ditch filters (Dayton and Basta, 2005). There have also been early experiments with the application of adding PSMs directly to eutrophic waters (Higgins et al, 1976). These experiments showed that lime was effective at phosphorus sorption, and fly ash gypsum was also effective, but only when co-applied with lime in order to raise the pH. That early study recommended looking into iron and aluminum salts, but concluded with the prohibitive cost of transporting enough gypsum to make a measurable difference in soluble P through this application method. Another early study proposed adding fly ash amendments to lake sediments to inhibit release of phosphorus during anoxic periods, which proved to be successful, but there were concerns about the release of heavy metals into lakes (Theis and McCabe, 1978).

The method of applying PSMs to vegetated buffer strips has had mixed results. A comparison of these studies shows that WTRs have the capacity to sorb all the phosphorus in the field runoff when those WTRs had similar amounts of Al and Fe oxides. However, some studies have shown the buffer strips to be highly effective in soluble P removal (Dayton and Basta, 2005), while in another study there were no appreciable differences between amended and non-amended buffer strips. It has been hypothesized that the application of PSMs must assign more emphasis to the retention time, as while some P sorption can be rapid, it generally must be longer than the ~30 seconds it took for runoff to flow over buffer strips in that study (Wagner et al, 2008). This observation drives home the idea that the construction of structures designed to remove soluble P from water must incorporate a means to maintain a sufficient retention time for

sorption to occur. It has been suggested that when one is measuring total phosphorus sorption capacity, the retention time must be at least 24 hours (Nair et al, 1984).

Applying PSMs directly to fields has the object of converting the P in fertilizer from soluble P to other forms, notably inorganic orthophosphate. The hypothesis is that the level of P that is plant-available would remain nearly constant, while the percentage of P susceptible to erosion would decrease and, even if that P entered waterways, would be less bioavailable to algae (Dou et al, 2003; Dayton and Basta, 2005). Co-applying WTR with biosolids has been shown to reduce P when fertilizer was applied at N-based rates without increasing dissolved Al in groundwater (Agyin-Birikorang et al., 2009). Brown and Sartain (2000) found that a 2.5% by weight addition of Fe-based WTR to biosolids decreased P leaching while minimally impacting P uptake by plants. Ippolito et al. (1999) reported that a ratio of 8:1 WTR to biosolids would maximize the sorption of soluble P, but that a higher ratio would result in P deficiency in crops.

Application of PSMs to poultry manure reduces the potential for P loss by decreasing water solubility of soil P (Warren et al., 2006). However, there is some evidence that using PSMs to change the form of P in the soil may not be sufficient to reduce P loss long-term, as much of the converted P, while not soluble, is still bioavailable to some extent (Dao et al, 2005).

Mixing WTR with soils has been shown to increase the maximum P sorption (Pmax) of coastal plain ultisols from <1 mg P/g to 1.7-8.5 mg P/g, with the implication that increasing the maximum P sorption capacity of the soil would result in a reduction in P loss from those soils (Novak and Watts, 2004). It should be noted that the soils tested were already very high in soil P and were nearing their maximum sorption capacity. It can be inferred that soils that are not near the maximum sorption capacity would not show an appreciable decrease in P loss due to this mechanism.

In an incubation study, it was found that the addition of PSM materials, and especially gypsum, was up to 63% effective in reducing P desorption from spodosol soils that contained large amounts of organic matter from the dairy industry (Anderson et al. 1995). Application of PSMs to cattle loafing areas resulted in a lower P concentration in runoff water, but the effects disappeared after several weeks indicating that the application was not an efficient management practice (Penn and Bryant 2006) Also, the application of basic slag or fly ash to paddocks was shown to be fatal to cattle if they were allowed to graze in those paddocks too soon after application (Dewes et al. 1995).

Melter slag and other electricity plant byproducts have been used as backfill for tile drains in New Zealand for the past two decades, and there is currently work being done to optimize mixtures of these byproducts so that they do not release significant amounts of heavy metals into the ecosystem or raise the pH of the drainage water to unhealthy levels (McDowell et al. 2008).

Finally, there have been efforts to install structures in drainage ditches designed to force ditchwater with a high P load through a PSM layer before it enters a larger waterway (Penn et al, 2007). This method of application has the benefit of concentrating the PSM in one place and only having to apply it once in several years. One of the PSMs being used in this method is synthetic gypsum, which has a high sorption capacity, but is too finely textured for quick flowthrough during storm events.

Effects of Hydraulic Flow on P Sorption

It has been found in numerous studies that soils that have a high percentage of fine silts or clays have a greater phosphorus sorption capacity than sandier soils (Bruland and Richardson, 2004). One clear explanation for this phenomenon is finer-textured soils tend to have greater

amounts of available Al and Fe than coarser-textured soils. Another explanation is as phosphorus sorption requires a certain residence time (Nair et al., 2004) suggested 24 hours for laboratory small batch experiments), the lower sorption seen in coarse-textured soils may also be partially explained by the greater hydraulic conductivity of those soils letting the phosphorus go through too fast for complete sorption (Fuchs et al, 2009). Besides texture, the presence of macropores has also been shown to increase P leaching by bypassing most of the soil matrix through preferential flow channels (Djodjic et al, 2004). It should be noted that Djodjic et al (2004) found total leachate volume did not increase in direct relation to coarser-textured soils, but rather found the arrangement of the soil within the columns to be of greater significance. Fuchs et al (2009) used coarsely textured soils (up to 80% of particles >2mm) in a study on P leaching, and found that small fractions of highly sorptive materials within coarsely textured soils can significantly reduce P leaching in the absence of preferential flow. However, it was found that preferential flow paths can negate any potential P sorption capacity. Another salient note was made by Leader et al (2008) when they observed that while finely-textured particles can be an important addition in terms of increasing surface area and cation exchange capacity, they are susceptible to erosion.

Kinetics

Phosphorus sorption has been shown to consist of three basic phases: a fast initial phase, a slower adsorption phase, and a plateau stage that can even lead to desorption (Appan and Wang, 2000). Most of the total phosphorus sorbed is sorbed in the initial stage, which can last from less than 30 minutes to as long as four hours (McDowell and Sharpley, 2002; Leader et al, 2008). Depending on the materials and conditions, this pattern can follow a linear or a nonlinear equation. Many studies on the sorption capacity of PSMs favor use of the Langmuir isotherm, as

it gives an estimate of the maximum sorption capacity and tends to fit the data better than the Freundlich isotherm (Cucarella and Renman, 2009; Rentz et al, 2009). In long-term studies, phosphorus sorption has been observed to consist of two phases, a rapid phase over roughly the first four weeks, followed by a slower phase over the next ~6 months. These phases are thought to correspond to the initial saturation of phosphorus sorption sites, followed by the slow conversion of phosphate minerals from more to less soluble forms (Ippolito et al, 2003).

It has also been reported that the results of batch studies on sorption characteristics of different PSMs can vary greatly on non-material related parameters such as initial P concentrations and material-to-solution ratios (Nair et al, 1984; Barrow et al, 2000; Cucarella and Renman, 2009; Stoner et al, 2012). A full-scale kinetics study would thus optimally have a wide range of batch parameters in order to present the kinetic behavior of phosphorus sorption under a variety of conditions. Barring this possibility, there are certain standard procedures suggested by Nair et al (1984) that could be followed. These standard procedures have the additional benefit of ensuring results amongst different labs can be compared.

A kinetic analysis of the addition of P as a chemical versus as a biological fertilizer (turkey litter) showed the resultant decrease in soil P sorption capacity was less in the case of the biological fertilizer (Brauer et al, 2007). An explanation suggested for this behavior is that the additional organic carbon being added with the turkey litter provided extra P sorption sites that were not present in the chemical fertilizer. Another possible explanation is that manure addition changes soil chemistry in a way that frees up extra calcium binding sites. Further kinetic analysis of these complex interactions is necessary to identify what is happening in the interface between soil and organic fertilizer.

Temperature Basis of Kinetics

While there have been relatively few studies on the effect of temperature on P sorption, it is known that wastewater treatment wetlands are less effective during the winter months, when there is nutrient release from soils (Malecki-Brown and White, 2009). Further, Appan and Wang reported that while phosphorus sorption constants in a tropical environment were similar to those found in temperate regions, the tropical environment displayed higher adsorption capacities (Appan and Wang, 2000).

In the laboratory, a PSM combination of iron oxides and waste eggshells was tested for phosphate sorption at temperatures varying from 20°C to 45°C and found that phosphate adsorption increased with temperature (Yeddou et al, 2009). Studies such as this have shown that the sorption of phosphorus is endothermic, and thus reaction rates should increase with increased temperature.

In a field study, Mamo et al (2005) found that there is a potential for increased P leaching through coarsely-textured soils if P-containing wastewater is applied during the winter months when the soil is cold, but not frozen. Other factors were noted that were more indicative of the potential for P loss, especially the relationship between the amount of P in the wastewater and the P already in the soil, determined whether or not the soil acted as a source or a sink of P in subsurface flow.

Summary

There is a need to reduce the amount of P entering our waterways, as eutrophication is already a problem and will only get worse as soils near their sorption capacity. Drainage ditches are one particular target of interest in terms of intercepting P before it gets to waterways because they represent the confluence of surface flow from entire fields as well as a fair amount of

subsurface lateral flow. PSMs have the potential to sorb most if not all of the excess phosphorus coming from fields, but can have side effects such as altering pH and releasing contaminants. Efforts should be made to utilize the opportunity presented by drainage ditches by incorporating PSMs into management strategies to prevent P loss. Maximizing PSM efficiency must take into consideration the P sorptive capacity, adequate retention time, and properly addressing the problems presented by temperature and preferential flow in soils.

Objectives

The goals of this research are: 1) to determine the effect temperature has on the efficacy of PSM phosphorus sorption, 2) to determine how different types of gypsum effect the sorption of P in a flow-through setting, 3) to determine how different types of gypsum and the inclusion of varying percentages of sand affect the hydraulic properties of a PSM column, 4) to determine the mixtures of gypsum and sand with the optimum relationship between sorption and hydraulic properties.

Chapter 2 – Materials and Methods

Isotherm Determination of Kinetics

An isotherm study was conducted to evaluate the effects of temperature on the adsorption of phosphorus by six types of phosphorus sorbing materials. The six types of phosphorus sorbing materials were 1) a mined gypsum from Nova Scotia that was coarsely ground and provided locally by US Gypsum Corporation in Baltimore, MD; 2) a finely textured gypsum produced from flue gas desulfurization (FGD) at the Conemaugh Generating Station, a coal-fired power station owned and operated by Reliant Energy near New Florence, Pennsylvania; 3) naturally formed acid mine residuals (AMDR) obtained from acid mine drainage flowing through an old well in Farmington, PA; 4) steel slag obtained from a plant in Pittsburgh, PA; 5) soil from the A horizon of a Hagerstown Series (fine, mixed, semiactive, mesic Typic Hapludalfs) located in a field that had not been fertilized with P for over 80 years near Keedysville, MD (39.51,-77.74); and 6) soil from the B horizon of the same Hagerstown soil located at the same site. For the sake of simplicity, these phosphorus sorbing materials will be identified as natural gypsum, FGD gypsum, AMDR, steel slag, the A horizon soil, and the B horizon soil, respectively. Photographs of each phosphorous sorbing material are presented in Figure 1a-f.

Material Characterization

Each material was sieved through a 2-mm sieve prior to all characterizations. Sand grain particle size analysis was performed through shaking 250 g of each sample on a set of sieves with successively smaller opening sizes for fifteen minutes. Silt and clay fractions were analyzed using the hydrometer method. pH levels and the ability to maintain a pH greater than 6.0 were determined using an Accumet AB15 pH meter, and titrating 10 g material in 50 mL of

DI water to pH 6.0 using HCl solution (concentration dependent on material). Acid digestion for total metal analysis (Ca, Fe, and Al) was conducted according to the EPA 3050B method (USEPA, 1996).

Isotherm Methods

Each material was air-dried and then sieved through a 2-mm sieve. Two grams of each material were weighed into each of eight 50-mL centrifuge tubes. Thirty mL of each $P_{initial}$ solution at concentrations of 0, 5, 10, 50, 100, 500, 1500, and 3000 mg P/L was added to each of eight tubes for each material plus a blank was included for each $P_{initial}$ level for a total of 56 tubes per run. A set of the tubes consisting of all material and concentration combinations was randomly placed in an end-over-end shaker in one of three temperature-controlled growth chambers for 24 hours at temperatures of 3°C, 13°C, and 23°C. After 24 hours, the tubes were centrifuged at 2000 rpm for 13 min and the supernatant filtered through 0.45-µm membrane filters under vacuum filtration. The filtrates were analyzed for phosphate-P concentration using the molybdate blue method on a Lachat QuickChem 8500 Flow Injection Analysis System (Hach Company, Loveland, CO) by the methods of Murphy and Riley (1962). Three replications of the sorption procedure were completed sequentially.

Langmuir parameters K and S_{max} (P sorption maximum) were estimated by plotting the solution equilibrated P concentration/P sorbed against the solution equilibrated P concentration for each material/temperature combination. The slope of this plot is $1/ S_{max}$, while the Y intercept is $1/ S_{max} *K$ (Essington, 2004).

Figure 1a: Coarsely ground gypsum

Figure 1b: FGD gypsum

Figure 1c: Acid mine residuals

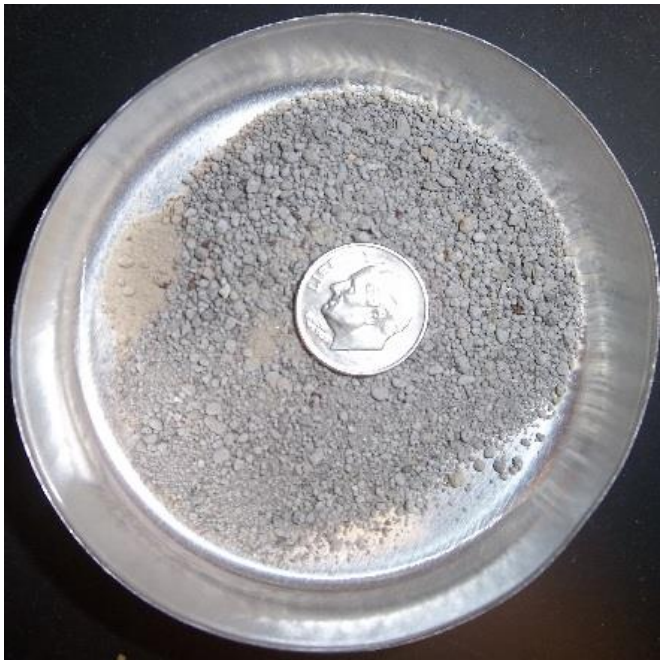


Figure 1d: Steel slag

Figure 1e: Hagerstown A

Figure 1f: Hagerstown B

Column Leaching Study

A laboratory column leaching apparatus was constructed that allowed the saturated hydraulic conductivity of phosphorus-sorbing materials to be determined (Fig. 2). Seventy-two 10-cm diam. PVC columns that were 76 cm in length were placed within racks for holding the columns vertically.

A study using the leaching apparatus was designed to determine the effects of different gypsum and sand mixtures on the resulting hydraulic conductivity of the materials placed within the columns. The study was designed as a completely randomized design with two types of gypsum, three gypsum / sand mixtures, and three levels of hydraulic head as the treatment factors. The two types of gypsum used were the coarsely ground natural gypsum (CG) and the FGD-derived synthetic gypsum (FGD) described earlier for use in the isotherm study. These materials were mixed with golf course sand in the proportions described in Table 1 to prepare the six mixtures. The golf course sand was found to have a small amount of iron oxides (18 g/kg

Fe), but will be treated as chemically inert for the purposes of this analysis. The three hydraulic head levels were 8 cm, 12 cm, and 16 cm. Three replications of each treatment were used in the laboratory evaluation.

Mixtures Used			
Mixture	% Coarse Gypsum	% FGD Gypsum	% Sand
CG	100	0	0
CG10	90	0	10
CG20	80	0	20
FGD	0	100	0
FGD10	0	90	10
FGD20	0	80	20

Table 1: Mixtures used in the hydraulic conductivity evaluations were CG (coarse gypsum) and flue gas desulfurization gypsum (FGD) combined with the stated proportions of golf course sand.

The gypsum materials were dry sieved to determine the range of particle sizes present in each material. The FGD gypsum was very uniform and had a silty texture (Bryant et al, 2012). The coarse gypsum had a roughly bimodal distribution of particle sizes according to Table 2. Any fragments greater than 10 cm in any dimension were removed from the coarse gypsum.

	% by Weight		
Particle Size (mm)	CG	FGD	Sand
> 25	21.4	0	0
25 < 10	21.4	0	0
10 < 5	7	0	0
5 < 2	8	0	0
0.425 < 2	13.3	0.4	12.1
0.25 < 0.425	10.2	1.0	57.1
0.075 < 0.25	17.9	35.7	30.5
< 0.075	0.8	63.0	0.3

Table 2: Distribution of particle sizes within the materials used as determined by dry sieving the material.

Coarsely ground gypsum (Figure 4a), FGD gypsum (Figure 4b), and golf course sand were air-dried and mixed according to treatment level in a 3.5 ft^3 Northern Industrial

Construction cement mixer and poured into 75-cm long, 10-cm diameter polyvinyl chloride (PVC) tubes. The mixtures were weighed and added one liter at a time, the tube was tapped with a rubber mallet, and the top of the mixture raked with a dowel after each liter addition of material. A uniform surface height of 50 cm at the beginning of the leaching period was desired. A non-replicated preliminary study was conducted using the gypsum / sand mixtures in Table 1. The mixtures were found to settle differently during the process of being wetted and water moving through the material. Based on the results of the preliminary study, the tubes containing all of the CG treatments were filled to an initial height of 55 cm, the tubes containing FGD filled to 72 cm, the tubes containing FGD10 filled to 69 cm, and the tubes containing FGD20 filled to 65 cm. These heights were calculated from the settling rates observed in earlier test runs using the same materials and treatment mixtures.

Mixture	Average Volume (cm^3)	Average Weight (kg)	Density
CG	4344	7.42	1.71
CG10	4567	7.48	1.64
CG20	4794	7.48	1.56
FA	5806	5.43	0.94
FA10	5828	5.42	0.93
FA20	5639	5.95	1.05

Table 3. The average volume, average weight, and density of the materials after settling for each of the mixtures.

The materials were retained within the columns by a layer of Reemay polyester landscaping material atop a perforated plastic plate at the base of each column. The columns were then capped on the lower end with a valve and vinyl tube attached for effluent collection. The caps were water sealed with a thick layer of vacuum grease and pushed onto the columns by hand. Each PVC column had a vertical series of 2.5-cm diameter holes in the front spaced 5 cm from each other to allow for vertical core sampling after leaching had concluded. These holes were sealed with screw-in plugs wrapped with Teflon tape.

Racks of the PVC columns were attached to a pump system that supplied a constant concentration of 2.4 mg/L phosphorus solution to each column (Figure 2). The solution was made by adding a 1000 mg/L phosphorus solution (made using 99.7% pure potassium phosphate dihydride) to tap water using a mixing manifold and injection pump to maintain proper concentrations (Figure 3).

The phosphorus mixing system was activated by a column float switch inside a 660-L delivery tank, which stored the 2.4 mg P/L solution prior to being delivered to the surface of the packed columns. When the contents of the delivery tank dipped below 300 liters, the pump located inside a 660 liter tap water storage tank was activated, pumping tap water through the mixing manifold into the delivery tank. This water flow activated the Lincoln Motors 0.5 hp injection pump which operated at a frequency of 20 Hz. The injection pump drew from a 380-L Agri-Inject tank containing a 1000 mg/L phosphorus solution which was constantly being agitated with a mixing wane. Finally, a ball float in the tap water tank activated a value that allowed tap water from the building water supply to enter the tap water storage tank.

A column float switch inside a 10-cm PVC pipe within the 660 liter P-solution tank activated the injection pump to enable the delivery of approximately 170 liters of mixed phosphorus solution at a time and was found to be the storage amount necessary to maintain homogeneity of the P solution. This P solution was supplied to the gypsum columns through three different feed tubes maintaining pressure heads of 8, 12, and 16 cm to specified columns. The solution entered the columns through hoses leading from the feed tube that emptied out into the column at a height of 55 cm.

After the dry mixtures were added, the columns were saturated from the bottom with tap water at the rate of 2.5 cm/hr until they reached the top of the material inside. This method of

wetting was used to slowly force air from the columns and minimize disturbance to the structure of the materials inside the columns. The materials were allowed to settle for six days, and the water inside drained to a height of 50 cm, which was the expected surface height of the materials within each column after settling. Ten mL of 1000 mg/L bromide tracer were added to the top of each column by pipette. Each column was filled to its assigned pressure head with the P solution and the valve on the bottom opened. All effluent was continuously collected into 19-L collection buckets, which were weighed and emptied every two hours for two days. A 50-ml sample was taken with each weighing. It was thought that the majority of the bromide would move through the columns within the first two days and that the initial breakthrough of phosphorus might also occur during this time period. After the initial sampling period of two days, the total quantity of effluent was no longer collected and weighed. Three-way valves were used to direct the effluent into a common drain pipe for disposal or into 19-L collection buckets for two-hour sampling periods, which occurred every six hours for two more days, every eight hours for the next three days, and finally every twelve hours for a final seven days, resulting in a total sampling period of fourteen days. The P solution entering the feed tubes was also sampled at each one of these sampling times.

A short time after obtaining the effluent samples, they were acidified to a pH of 2.0 with 1:1 nitric acid and divided into two subsamples (one of which was vacuum filtered immediately with 0.45-µm filter paper) and refrigerated. The filtered subsamples were analyzed colorimetrically for soluble phosphorus (Vadas et al, 2005) using a Technicon autoanalyzer using the molybdate blue method (Murphy and Riley, 1962, Mozafarri and Sims, 1996, Rhoton and Bigham, 2005). The unfiltered subsamples were tested for phosphorus, calcium, and sulfur by Technoflame ICP (Elliott et al, 2002a; Dou et al, 2009, Fuchs et al, 2009). Since it was found

that microwave digestion did not affect ICP results utilizing a test group of samples, a simplified procedure of adding 0.6 mL concentrated nitric acid to 10 mL unfiltered leachate sample was used (adapted from USEPA, 2001). The ICP analysis was thus done in a nitric acid matrix of 5.66%.

After the completion of the hydraulic conductivity measurements, the material remaining in each column was sampled by taking 0.75-cm diameter cores every five centimeters in height along the columns for phosphorus analysis by ICP. The core samples were ground by hand with mortar and pestle so that the sample material passed through a 1-mm sieve. A test group of samples showed no effect from microwave digestion, so a simplified procedure was used. A subsample of 0.25 g of the gypsum material was weighed to the nearest 0.0001g, received 10 mL 1:1 nitric acid, allowed to soak, and then brought to 100 mL volume with deionized water. Phosphorus levels within these samples, having a 5% nitric acid matrix, were determined by ICP.

To determine the presence of the bromide tracer in the leachate, 1 mL of total ionic strength adjustment buffer was added to 50 mL of unfiltered leachate sample and those samples analyzed for bromide with an Orion bromide-selective electrode using a standard calomel reference electrode attached to a Fisher Scientific Accumet AB15 pH meter.

Figure 2: Racks containing the 10-cm diameter PVC columns. In the foreground is the 660-L tank for containing the phosphorus solution that is to be fed to the surface of each column.

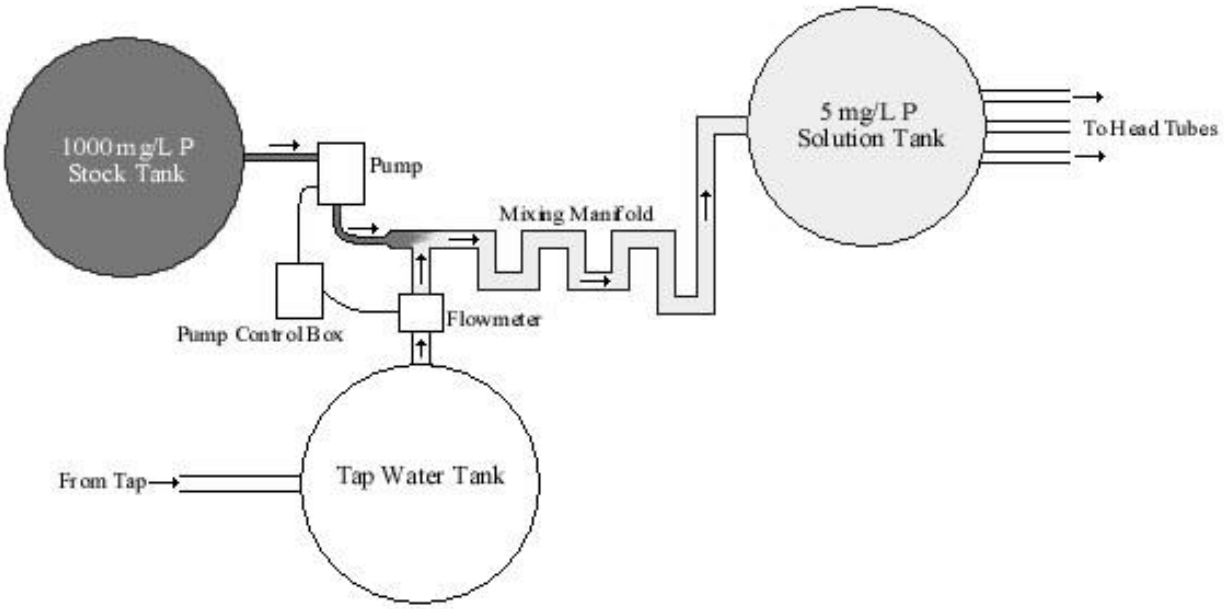


Figure 3: Schematic diagram of the storage tanks containing tap water, the 1000 mg/L stock tank, and the 5 mg/L solution tank. In the central area are the flow meter, the pump control box that monitors the flow of tap water through the line and controls the rate of stock solution injection into the line, and the mixing manifold that mixes the injected solution with the tap water within the line prior to pumping it into the solution tank.

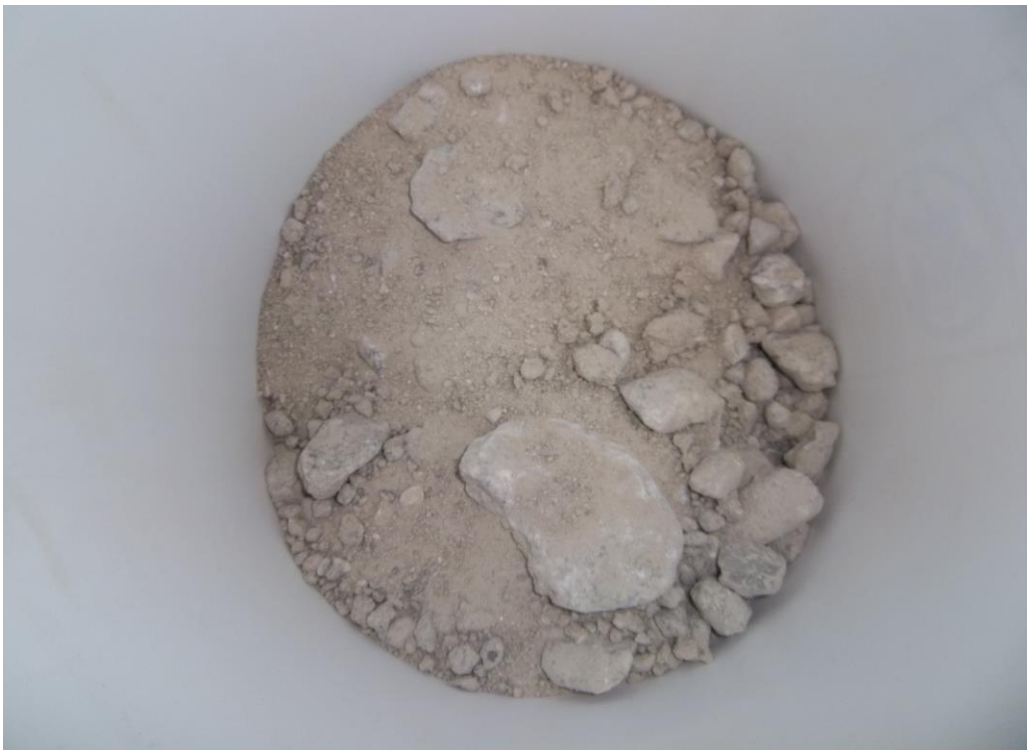


Figure 4a: Coarse Gypsum material prior to being sieved for removal of aggregates greater that 10-mm in any dimension.

Figure 4b: FGD gypsum material prior to use in the study.

Chapter 3 – Results and Conclusions

Isotherm Study

Material Characterization

	Material (% Weight)				
Sieve Size (mm)	Hag A	Hag B	Rock Gyp	FGD Gyp	Slag
2.0	0.0	0.0	0.0	0.0	0.0
0.85	1.9	1.6	10.9	0.0	4.7
0.425	2.5	1.3	16.2	0.3	31.5
0.25	3.2	2.7	21.4	1.0	13.4
0.15	10.5	6.6	19.4	4.7	4.3
0.075	2.2	3.7	18.4	31.0	1.7
Silt	62.7	58.3	13.8	63.0	2.1
Clay	17.0	25.8	0.0	0.0	0.0

Table 4: Particle size distribution of PSMs used, expressed as the percentage by weight that did not pass through each sieve in a series. Silt and clay fractions were determined by hydrometer.

Material	pH	Buffer Index (eq/kg)	Total Al (g/kg)	Total Fe (g/kg)	Total Ca (g/kg)
ADMR	3.2	0.0	1.6	88.1	301
Hag A	5.73	0.0	18	24.2	183.6
Hag B	5.52	0.0	16.2	26.3	142.8
Rock Gyp	7.72	0.03	19.2	38.3	245
FGD Gyp	7.88	0.09	10.5	2.1	236
Slag	11.31	0.75	26.2	204	271

Table 5: Chemical characteristics of PSMs used. Buffer Index: equivalents of acid kg^{-1} required to decrease pH to 6.0.

Temperature Effects on P Sorption

Although trials were completed up to an initial concentration of 3000 mg P/L, the extremely high levels of P both are unrealistic in a field setting and also interfered with the analytics. Thus, all trials with an initial P concentration greater than 500 mg P/L for the byproduct PSMs were not included in the analysis. When analyzing the soils, no initial P concentrations greater than 100 mg P/L were used.

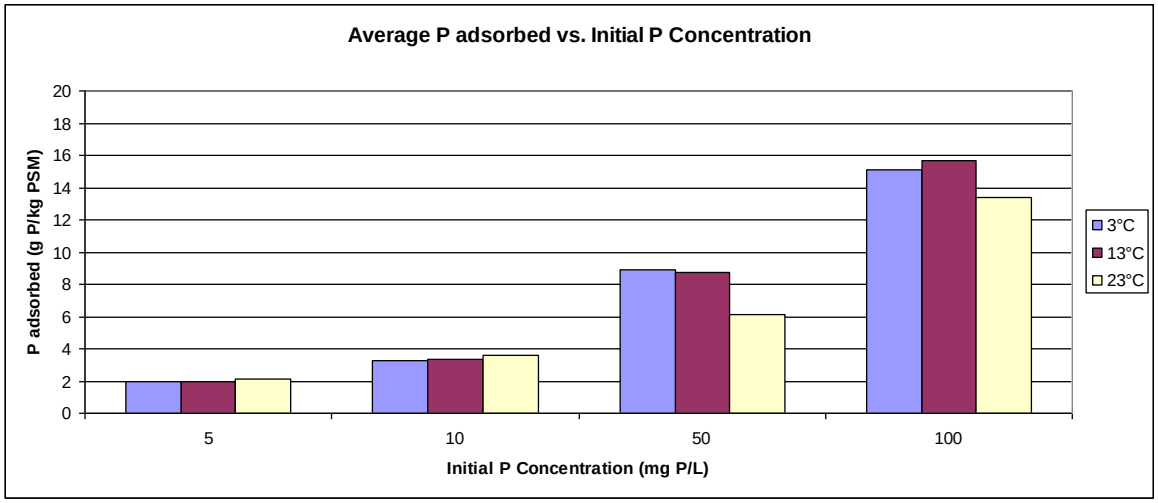
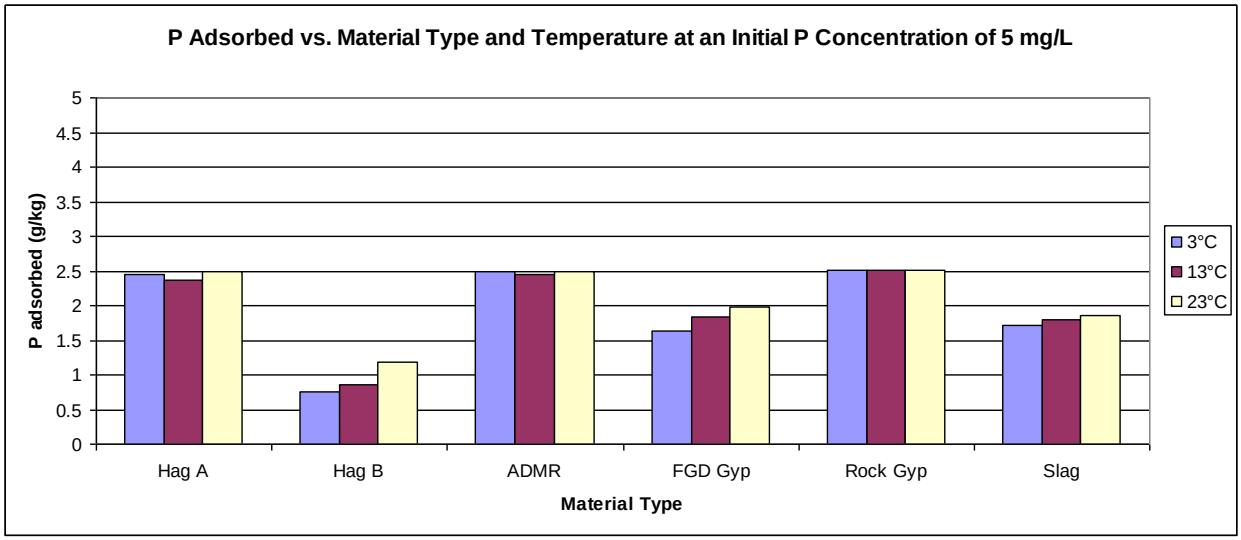
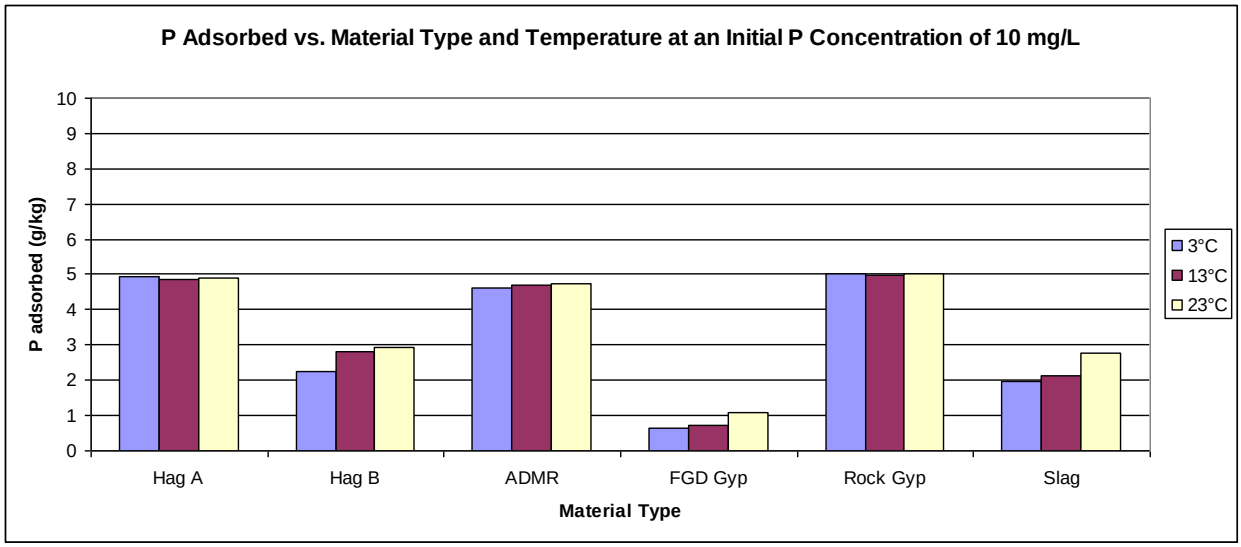
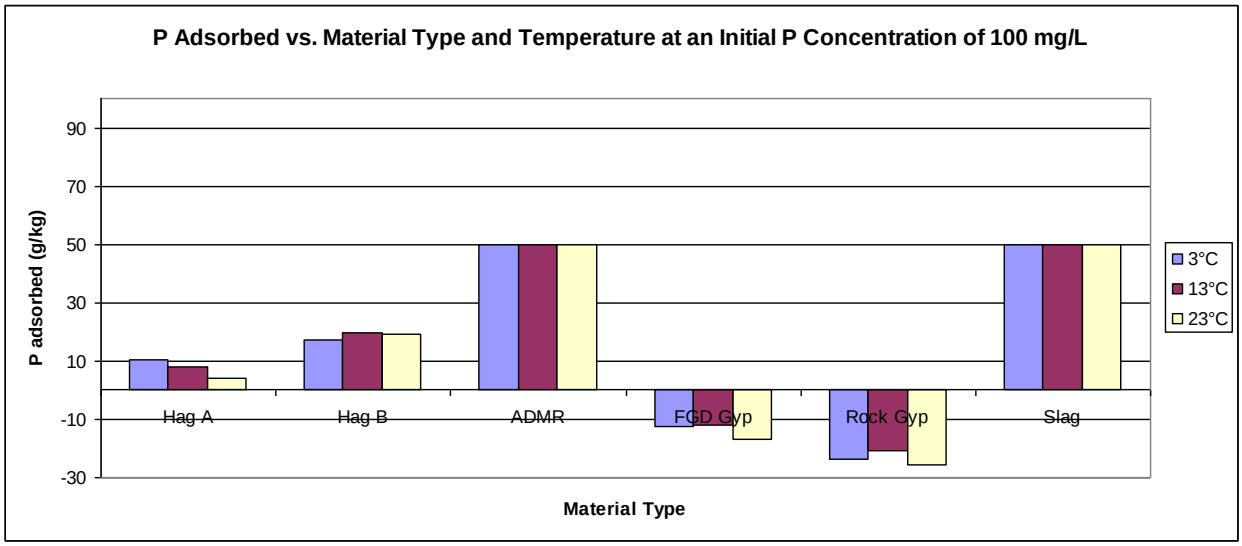


Figure 5: The effects of temperature on phosphorus (P) sorbed averaged across all phosphorus sorbing materials at initial P levels of 5, 10, 50 and 100 mg L^{-1}.

No significant effect of temperature was found when averaging across all PSMs tested. These isotherms used a 24-hour sorption period, a timeframe similar to common storm surge events. However, experimentation on PSM kinetics has found that several of these materials sorb phosphorus in a much shorter amount of time. Therefore, many differences in kinetic activity due to temperature would likely be seen in the first hour or two of sorption. By the time 24 hours have elapsed, several of the sorption materials may have reached equilibrium regardless of temperature-driven changes in kinetic rates. This is especially true of any Fe-based ligand exchange, which adsorption reactions with phosphate should be completed within a matter of minutes and be somewhat difficult to adequately characterize. Ca-based precipitation exhibits slower kinetics, but given the small quantities of material involved (2 g) and the large quantity of solution used (30 mL), equilibrium should be largely achieved within 24 hours regardless of temperature.







Figures 6a,b,c: Phosphorus adsorbed vs. material type and temperature at given initial P concentrations. The graphs are scaled so that % of initial P can be compared across graphs.

When examining each combination of PSM and initial P level individually, there remains no significant evidence that temperature has an effect on P sorbed.

Material Effects on P Sorption

(The PSMs and the soil horizons will be treated separately in this section, due to the difference in residuals.)

P Adsorbed by PSMs (mg P / g PSM)				
	Initial P Concentration (mg/L)			
Material	5	10	50	100
Hag A	1.8	2.6	4.4	7.4
Hag B	2.4	4.7	11.3	18.5
ADMR	2.4	4.9	24.8	49.7
FGD Gyp	1.7	2.3	-6.5	-14.1
Rock Gyp	0.8	0.8	-11.5	-23.5
Slag	2.5	5.0	24.9	49.8

Table 6: The amount P sorbed by the acid mine drainage residuals (ADMR), the Hagerstown A horizon soil, the Hagerstown B horizon soil, the mined gypsum (Rock Gyp), the iron slag material (Slag), and the synthetic gypsum (FGD gyp).

PSM	Temp (°C)	Lagmuir S_{max}	Langmuir K
Hag A	3	7.6	0.00009
Hag A	13	7.9	0.00015
Hag A	23	5.2	0.00040
Hag B	3	15.6	0.00056
Hag B	13	17.0	0.00051
Hag B	23	14.7	0.00080

Table 7: Temperature effects on calculated Langmuir coefficients for the Hagerstown A and B horizons.

Neither the A nor the B horizon of the Hagerstown soil exhibited a significant correlation between temperature and S_{max}.

The A horizon did however exhibit lesser S_{max} values than the B horizon at all temperature levels, which could be explained by a combination of the documented positive correlation between clay content and S_{max} and the negative correlation between soil pH and S_{max} (Kang, 2009).

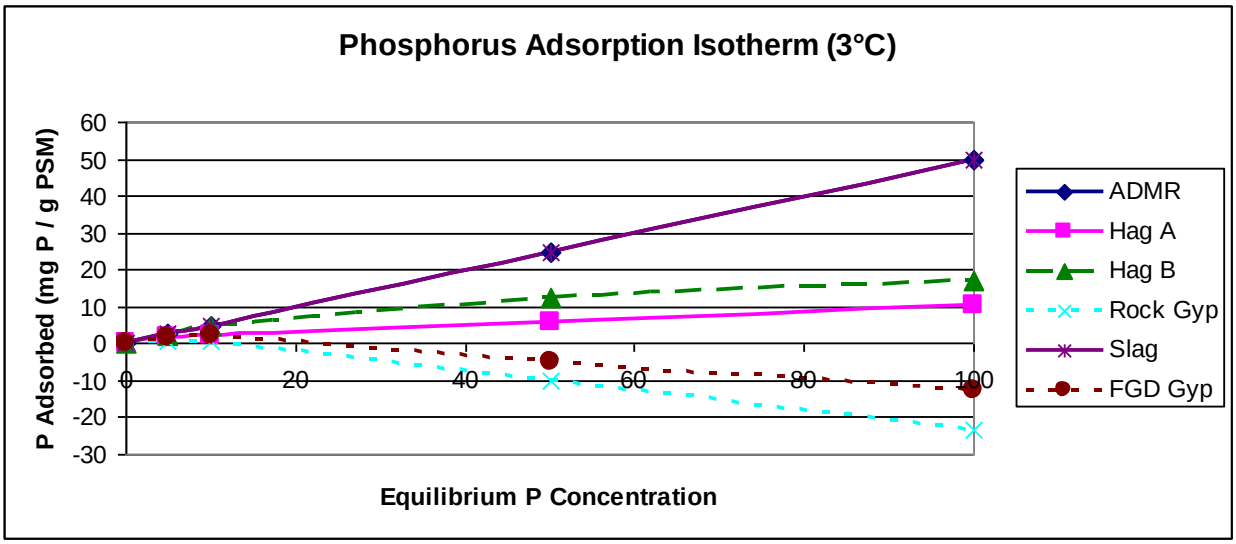
PSM	Temp (°C)	Lagmuir S_{max}	Langmuir K
AMDR	3	240.2	0.00045
AMDR	13	243.9	0.00034
AMDR	23	208.3	0.00054
FGD Gyp	3	2.1	0.00278
FGD Gyp	13	2.3	0.00264
FGD Gyp	23	3.5	0.00087
Rock Gyp	3	0.6	-0.00126
Rock Gyp	13	21.6	0.00001
Rock Gyp	23	0.0	0.00000
Slag	3	201.0	0.00090
Slag	13	190.3	0.00074
Slag	23	200.5	0.00094

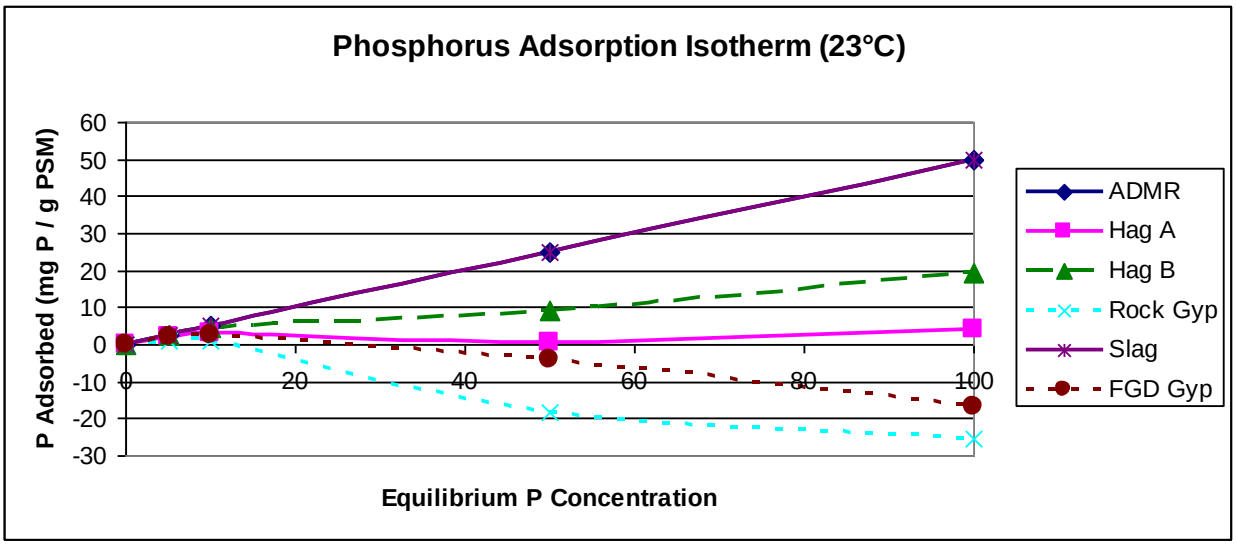
Table 8: Temperature effects on calculated Langmuir coefficients for the industrial byproduct PSMs.

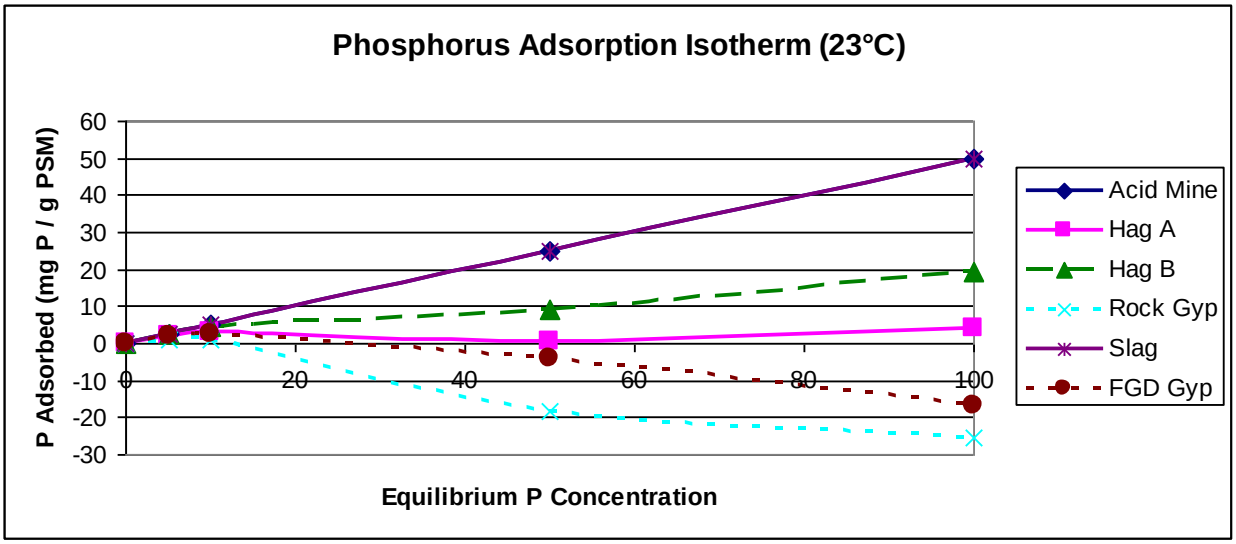
There was no significant difference in the Langmuir coefficients between temperatures in this case either. Again, a shorter timeframe may be necessary to capture any observable differences. One surprising result was the extremely low P sorption exhibited by both forms of gypsum. In most replicates with an initial P concentration of 50-100 mg/L, the results suggested desorption, which suggests that both kinds of gypsum already contained phosphorus that was released. Although the gypsums and slag are all Ca-dominated PSMs, the steel slag showed a greater initial pH as well as a much greater buffer capacity, which would explain the higher S_{max} values obtained for steel slag. ADMR, because of its low pH, would have sorbed P through surface complexation of Fe and Al (an exothermic reaction) rather than Ca precipitation.

On the other hand, a short-term series of isotherms such as these do not give a complete picture of the behavior of these materials in field conditions over a period of many months. Gypsum has regenerative properties for phosphate sorption that allow it to be a reliable PSM for low-flow, low P conditions over several years, as evidenced by the test ditch filter project in Princess Anne, MD (Bryant et al, 2012). The acid mine residuals may also see an increase in sorptive capacity given lower concentrations of P over a longer time. However, the contamination issues inherent in using acid mine treatment residuals remain, and while the cost

of transporting a dense material such as slag from a factory to a farm may remain high, it seems a viable PSM at all temperatures and concentrations. This study provides evidence supporting some concerns about the situational dependence of gypsum as a PSM, although those concerns can be partially alleviated with proper filter design that takes into account the strengths and weaknesses of this material as a phosphorus sorption material.







Figures 7a,b,c: Phosphorus adsorption isotherms for the acid mine drainage residuals (ADMR), the Hagerstown A horizon soil, the Hagerstown B horizon soil, the mined gypsum (Rock Gyp), the iron slag material (slag), and the synthetic gypsum (FGD gyp).

Limitations of the P Sorption Isotherms

Detailed data from this isotherm study can be found in Appendix A.

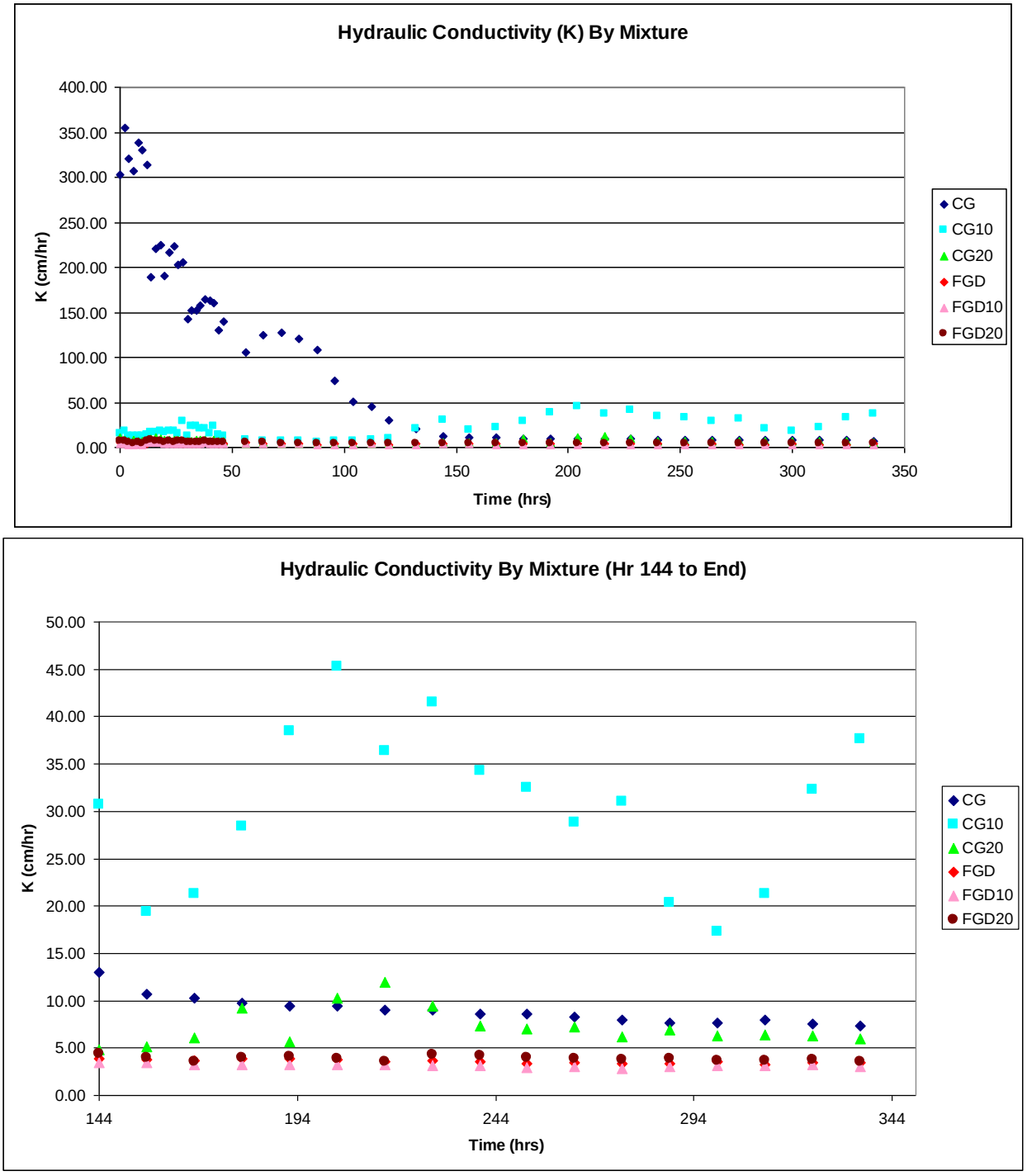
Column Study

Hydraulic Properties

(Chemical characterizations of the gypsums used can be found in Table 5)

The hydraulic conductivity (K_{sat}) of the experimental units was found to vary according to the gypsum/sand mixture used (Fig. 8). Furthermore, K_{sat} was found to vary significantly both as an instantaneous measure (measured at any given point in the study) and as a mean over the course of the experiment. This result is not unexpected considering the high variability in K_{sat} that soils routinely exhibit. The notable aspect of the instantaneous K_{sat} were the mixtures that displayed significant changes in K_{sat} throughout the experiment (Fig. 8).The CG mixture displayed different K_{sat} values during the initial five days of the study when compared to later in the study. The CG10 mixture displayed significantly different K_{sat} values in the latter part of the study as compared to the initial earlier values. The CG20 and FGD-type mixtures did not show any significant differences from each other during any part of the study, but amongst the mixtures incorporating FGD gypsum, the columns with more sand exhibited slightly higher hydraulic conductivities over the entire span (Figure 9). This trend suggested there may be a real increase in hydraulic conductivities with the use of larger percentages of sand than the percentages used in this study. It should be noted that because of the larger flow rates that accompany larger percentages of sand, experiments of this nature become exceedingly difficult to conduct in a laboratory setting. The variation in K_{sat} was likely affected by a number of factors, including the column height, particle sorting and thus the development of heterogeneity in the columns, changes in the crystalline structure in the column material, and the development of preferential flow pathways. Because of the inherent variability associated with the hydraulic

conductivity measurements of these materials, the different pressure heads used as a treatment effect were not found to be significantly different from one another (Appendix C).



Figures 8a,b: Averaged saturated hydraulic conductivities (k) of the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures over the measurement period, and also during the latter part of that period.

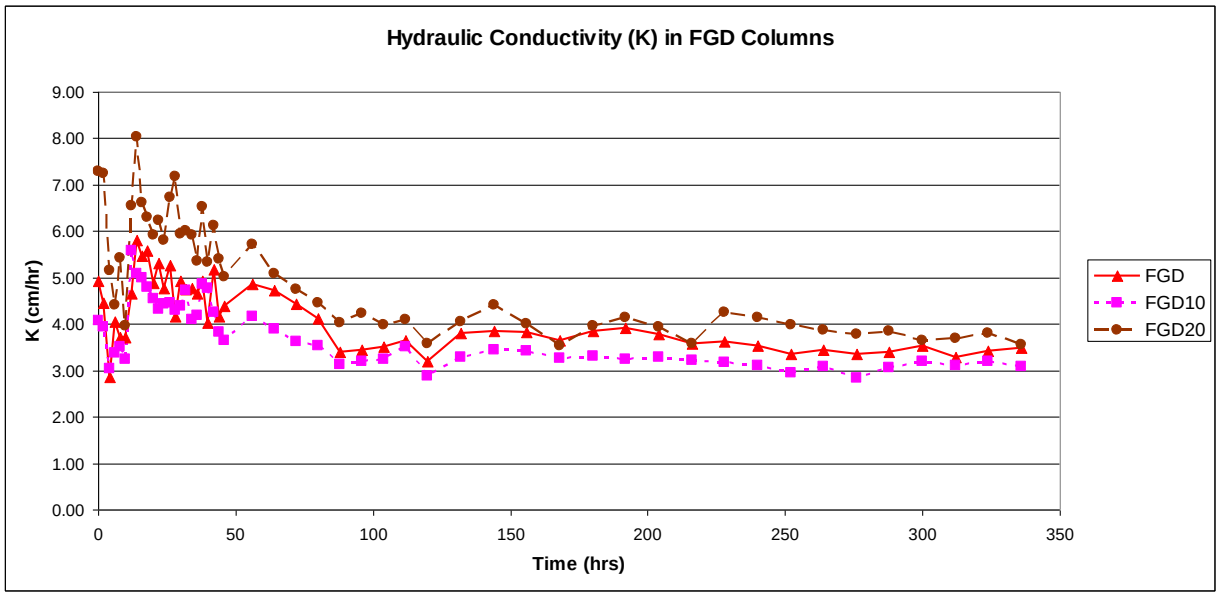


Figure 9: Averaged saturated hydraulic conductivities (k) of the FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures over the measurement period. The mean differences between these three different mixtures were not found to be statistically significant.

One potential reason for the lack of significance in pressure head was any differences would have been confounded by variation in the extent to which the mixtures settled within the columns. The average heights to which each mixture settled are given in Table 9.

Mixture	Minimum Height Lost (%)	Maximum Height Lost (%)	Average Height Lost (%)	Average Final Column Height (cm)
CG	11.4	27.3	20.7	43.6
CG10	8.0	38.6	23.5	42.1
CG20	6.8	27.3	12.0	48.4
FGD	29.8	31.6	30.7	49.4
FGD10	30.0	31.8	30.8	47.6
FGD20	23.1	30.8	24.9	48.8

Table 9: Average loss of column height for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

As the target final column height was 50 cm, the FGD-type mixtures settled approximately to the extent predicted by the test study. The CG and the CG10 mixtures settled far more than the predicted extent, due mostly to sudden collapses of the internal structure

observed in most of those columns. During the early part of the experiment, extremely high flow rates were observed in the CG and CG10 columns, which tended to suddenly and dramatically decrease (Table 10).

		Time (Hours Elapsed)									
		42	44	46	56	64	72	80	88	96	104
Mixture	Head	Outflow (liters)									
CG	**12 cm**	**28.02**	**29.14**	**33.86**	**9.14**	**7.08**	**5.24**	**4.70**	**4.14**	**3.66**	**3.64**
CG20	8 cm	1.18	1.52	1.14	1.04	1.00	0.82	0.86	0.78	0.80	0.80
CG10	8 cm	1.62	1.46	1.16	1.56	1.46	1.22	1.36	1.10	1.14	1.14
CG20	16 cm	1.44	1.54	2.46	1.22	1.24	1.08	0.80	0.78	0.86	0.80
CG	**16 cm**	**90.76**	**45.44**	**55.08**	**62.18**	**70.02**	**59.60**	**63.40**	**56.52**	**14.76**	**9.10**
CG	**16 cm**	**15.50**	**11.28**	**6.40**	**7.50**	**4.60**	**3.54**	**3.22**	**4.34**	**3.34**	**2.76**

Table 10: Portion of outflow data featuring sudden drop-offs in outflow in 3 of the CG columns.

At the same time that the outflow decreased, a sharp drop in the column height was observed. The extent of the drop varied between 9 and 18 centimeters. It is hypothesized that the particles in these columns were sorted by water movement, leaving the largest particles balanced on each other in the upper part of the column. As the edges of these large particles were slowly dissolved by water movement, the structure collapsed, both reducing the height of the column and at the same time collapsing the macropores that had to that point allowed extremely high rates of flow. By this mechanism, the extremely high flow rates such as those detailed were due to macropore flow, and the sharp decrease in flow rates exhibit a switch to matric flow similar to the flow pathways in the CG20 and FGD-type columns.. Those collapses were not observed in the CG20 columns, and it is hypothesized that the higher percentage of sand resisted the sorting seen in the columns with a more bimodal distribution of particle sizes. A result of these collapses on the experimental setup is that instead of the steps between pressure heads being 50% of the lowest level (8, 12, and 16 cm), the steps became 28-49% of the lowest level (14.4, 18.4, and 22.4 cm). A small difference between levels would be expected to minimize any effects pressure head may have on hydraulic conductivity.

In terms of the FGD mixtures, there was some evidence that there may have been preferential flow pathways due to wetting front instability even in these fairly homogenous mixtures. When the columns were disassembled after the experiment, it was noted that the upper 1-4 centimeters of the FGD columns (Figure 10) as well as some pores leading downward (Figure 11) were a darker color with a more brittle texture, but also featuring a very porous appearance. After several diagnostic tests, this material is believed to be an iron sulfide compound. Iron sulfides, while Fe-based, are not considered phosphorus-sorbing, as they do not adsorb phosphate at neutral pH levels and are known to even leach previously sorbed phosphorus as iron is reduced during their formation. As FGD gypsum is a pH-neutral to slightly basic PSM, any phosphate sorption is considered to be an effect of the calcium in the system rather than these iron sulfides.

Figure 10: Dark, brittle FGD material (left) compared to rest of column immediately below (right).

Figure 11: Close-up of disassembled FGD column showing evidence of preferential flow.

A further physical characteristic of FGD gypsum has been seen in the field, as the surface of ditch filters composed of FGD gypsum has undergone surface sealing, preventing P-loaded water from entering the PSM layer of the filter (Bryant et al, 2012). This sealing has been found to be a primary cause of an observed decrease in filter efficacy over time. It is possible that in addition to increasing hydraulic conductivity to a degree, the addition of sand could interfere with this sealing by keeping the gypsum particles farther apart.

Phosphorus Removal

During initial tests, the concentration of P in the water entering the columns was highly variable (a 2 mg P/L difference was typical). The pump control during these trials was a free-floating float that was highly sensitive, often turning the pump on for a few seconds at a time. It was hypothesized that this sensitivity did not allow the pump engine to warm up and deliver a reliable number of P solution injections over this short period of time. The free float was replaced with a float system on vertical pipes that delivered a minimum of 100 liters over several minutes to the P solution tank, which resulted in a more normalized solution P. During the

column study, the solution of phosphorus entering the columns was found to vary somewhat between 2.2 and 2.6 mg P/L water (Figure 12).

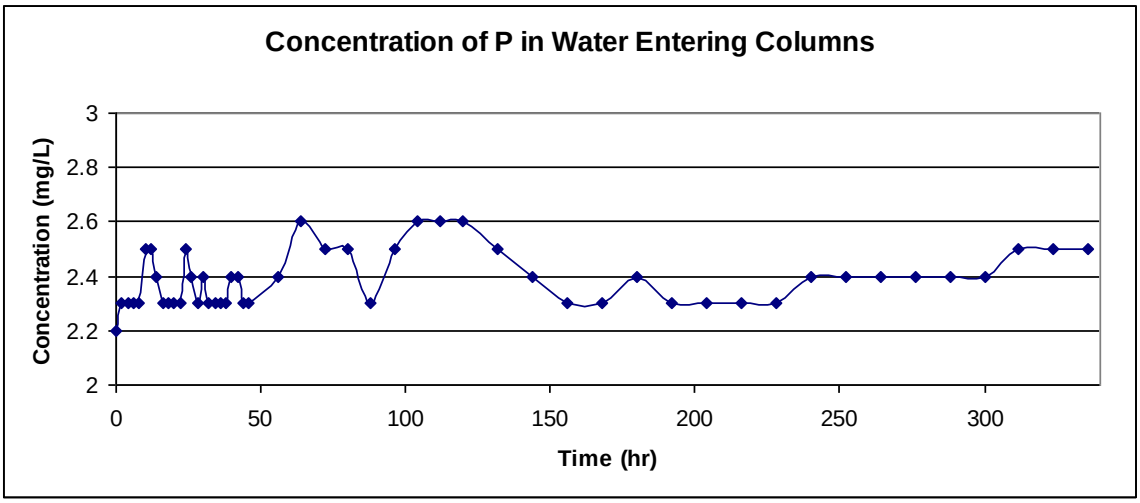


Figure 12: Concentration of phosphorus in the solution entering the columns.

The amount of phosphorus absorbed can be expressed in three different ways: percent of phosphorus entering the column that was retained by column materials, amount of phosphorus exiting the columns, and total phosphorus removed throughout the duration of the experiment. The retention rate showed two basic patterns, depending on if coarse gypsum or FGD gypsum was used. The retention rate in the columns containing pure coarse gypsum was characterized by extremely low retention in the first part of the experiment and then an increase in P retention that corresponded to a decrease in flow-through, while the FGD columns exhibited high initial P retention followed by rapid decreases in retention (Figure 13). The retention rates seen in the CG10 and CG20 mixtures were initially similar, with the CG10 mixture showing slightly higher P retention. However, beginning near hour 144, the CG10 mixture exhibited steadily decreasing P retention that corresponded with increased flow-through. The CG20 mixture exhibited steadily increasing P retention during the same period. By the end of the study period, the mixture that exhibited the highest percentage of P retained was the CG20 mixture, followed by (in decreasing order) FGD, FGD10, FGD20, CG10, and CG (Figure 14).

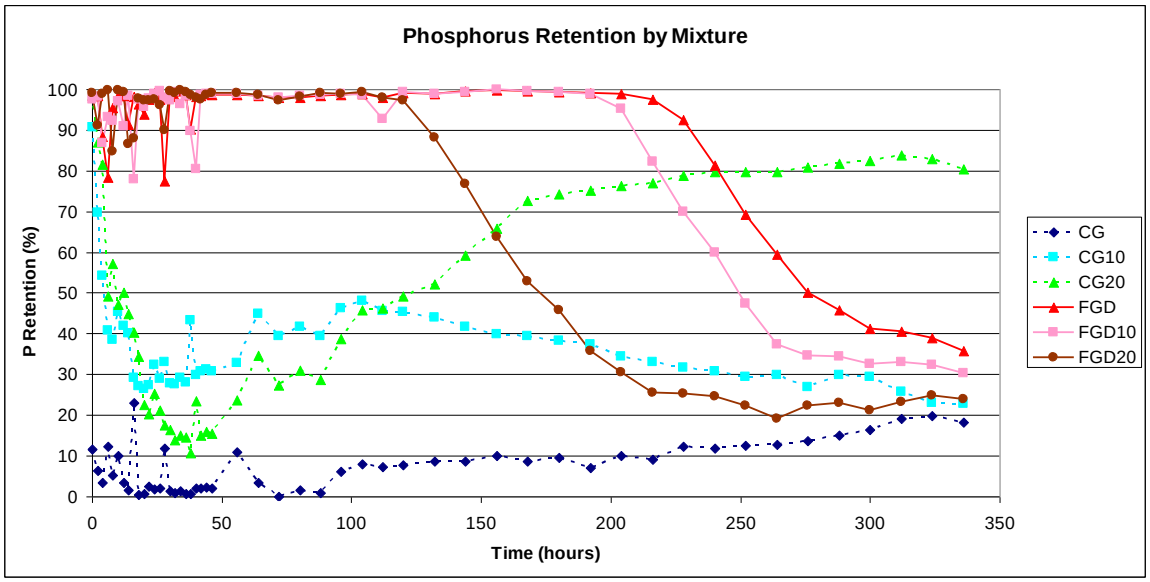


Figure 13: Averaged percentage of phosphorus entering the column that was retained by the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) columns during each sampling period.

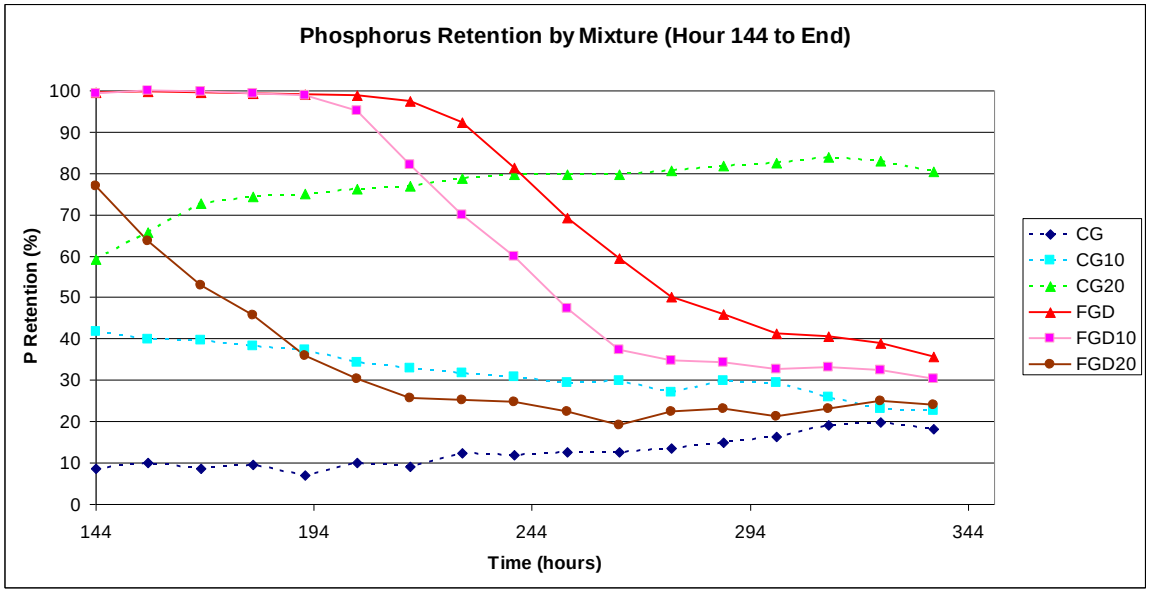


Figure 14: Percentage of phosphorus entering the column that was retained by the column during the latter part of the study.

Mixture	Porosity	Pore Volume (mL)	Flow Rate (mL/min)	Retention Time (min)
CG	0.36	1583	287	5.5
CG10	0.38	1703	1096	1.6
CG20	0.41	1835	221	8.3
FGD	0.65	3738	101	37.0
FGD10	0.65	3617	93	38.9
FGD20	0.60	3172	111	28.6

Table 11: Column characteristics related to retention time for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures. All values have been calculated from hour 144 to the end of the experiment, after the equilibration period.

Pore volume, average flow rate, and retention time (pore volume / flow rate) were calculated using the latter part of the study (Table 11) By this point, the columns had achieved an equilibrium regarding hydraulic properties (Figure 8b). The sorption reaction between gypsum and P is a relatively slow P sorption reaction, due likely to its poor buffer capacity (Stoner et al, 2012). According to the model for gypsum proposed by Stoner et al, retention time should be positively correlated with P removal, however only a very weak positive correlation was found (Figure 15). The weakness of the correlation may be due to the sealing and preferential flow discussed earlier.

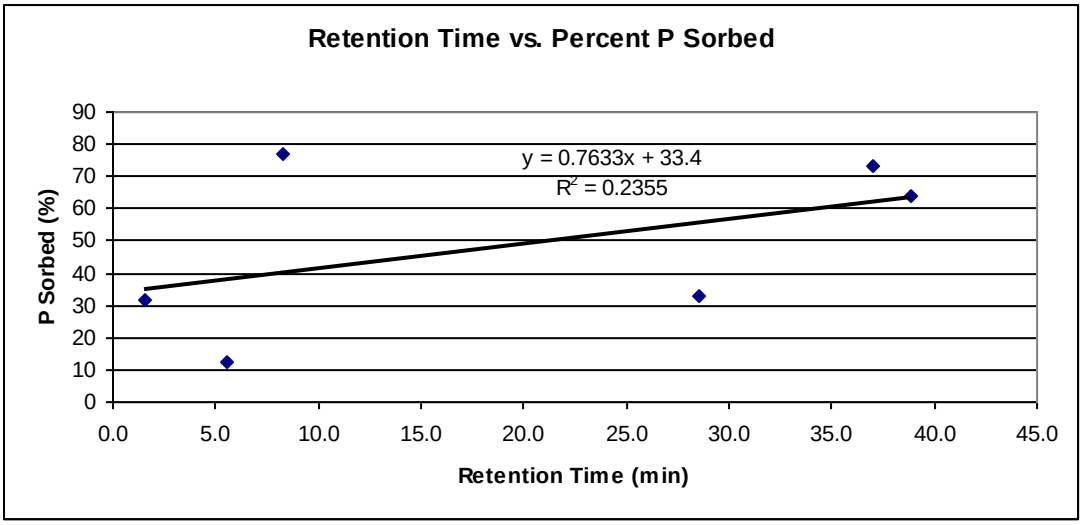
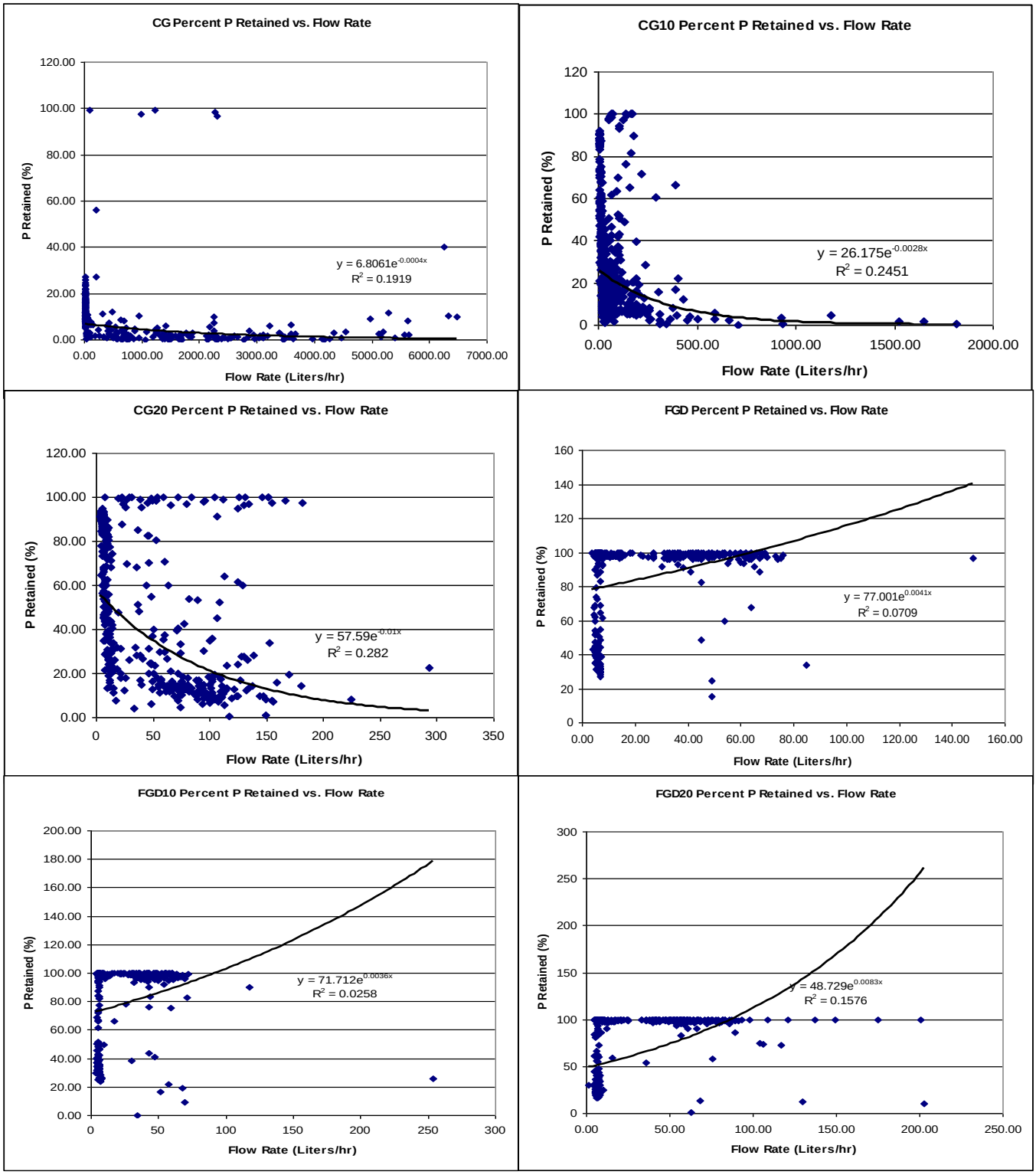
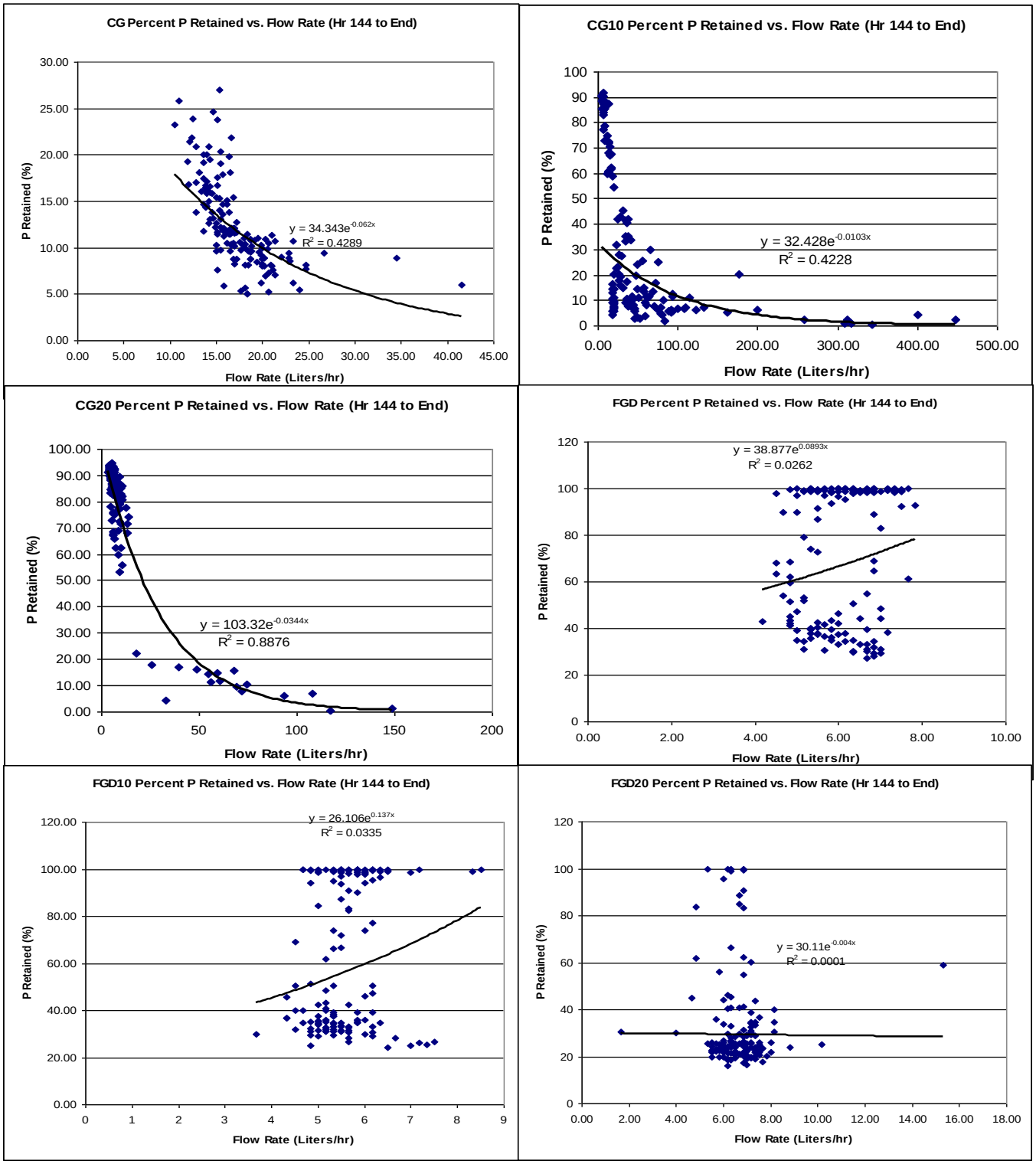


Figure 15: Retention time plotted against the percentage of P entering the column that was sorbed by the PSM.



Figures 16a-f:Percent of P flowing through columns retained by CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) columns plotted against flow rate.



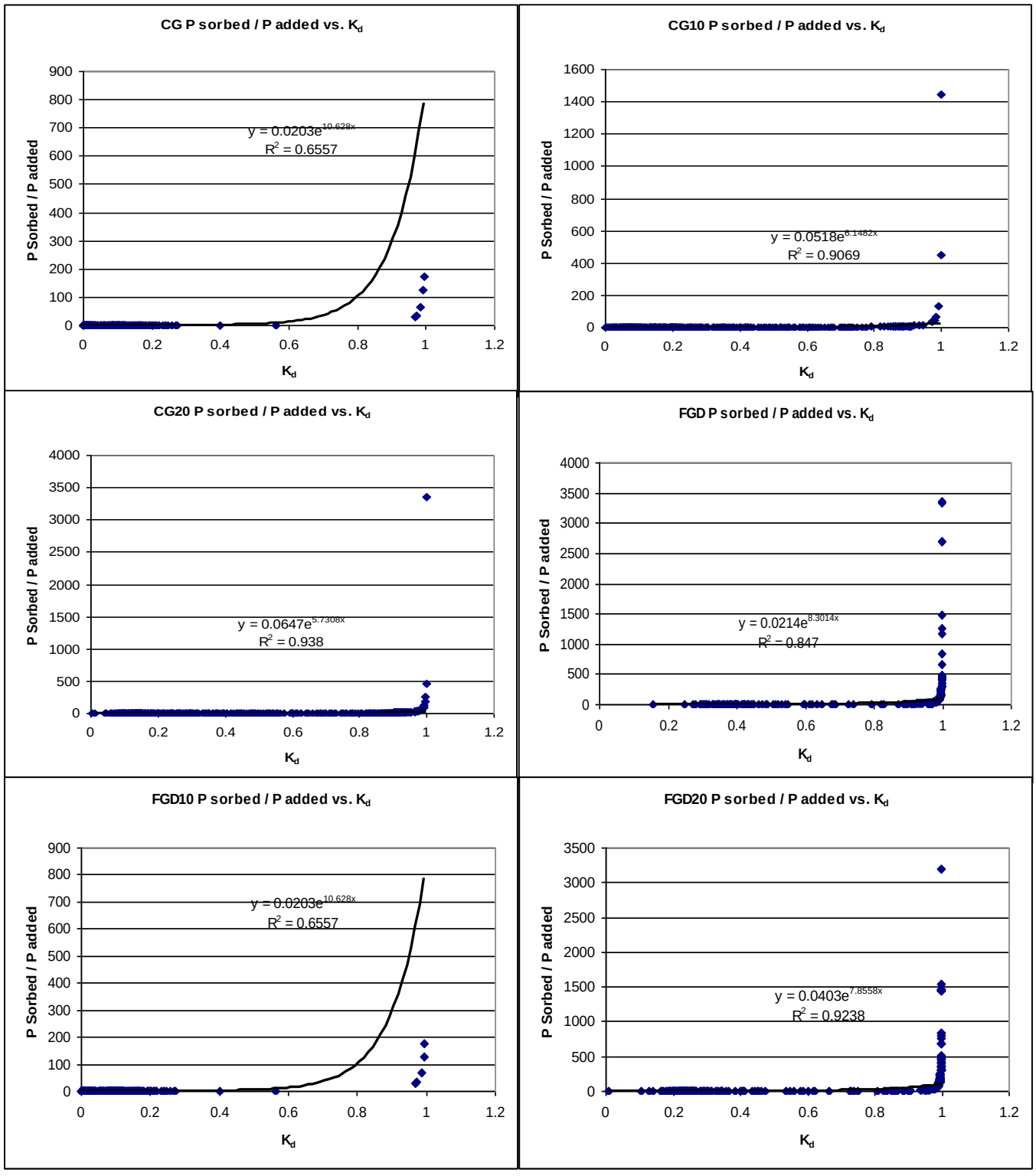
Figures 17a-f:Percent of P flowing through columns retained by CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) columns plotted against flow rate during the latter part of the study.

No significant correlation was found when comparing the percent of P entering the column that was retained versus the flow rate for the entire duration of the experiment (Figures 16a-f). However, in the latter part of the experiment weak negative correlations exist in the CG and CG10 mixtures, and a strong negative correlation exists for the CG20 mixture (Figures 17a-f). This indicates that the percentage of P retained by coarsely ground gypsum is adversely affected by higher flow rates once equilibrium conditions have been established. This is especially true of the CG20 mixture, which, possibly due to less PSM added, is most sensitive to a reduction in retention time.

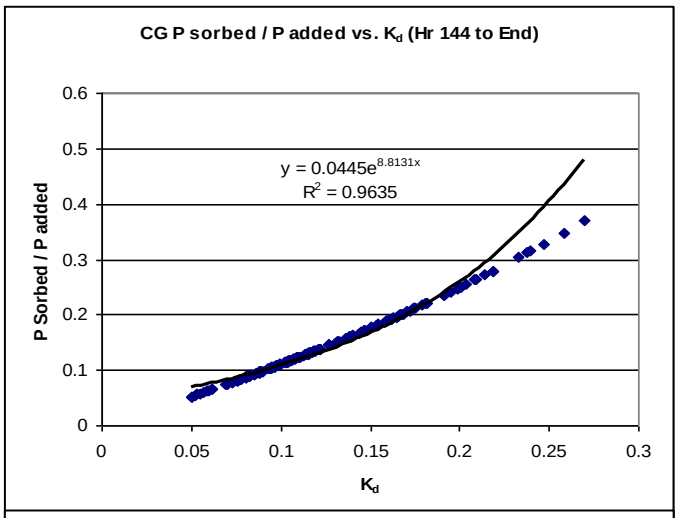
The amount of P retained per P added was then plotted against the partition coefficient K_d. There was a strong positive correlation between the two values for all materials (Figures 18a-f). The correlation was especially strong during the latter part of the study (Figures 19a-f).

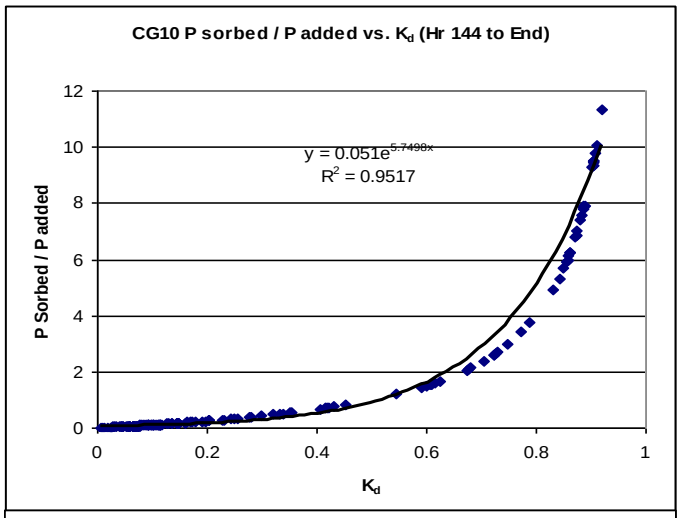
The efficiency of the columns in terms of mg P sorbed per gram PSM vs. flow rate was also plotted. However, no significant correlation was found in any of the mixtures (Figures 46a-f, Appendix C). This was also the case when analysis was isolated to the latter part of the study (Figures 47a-f, Appendix C).

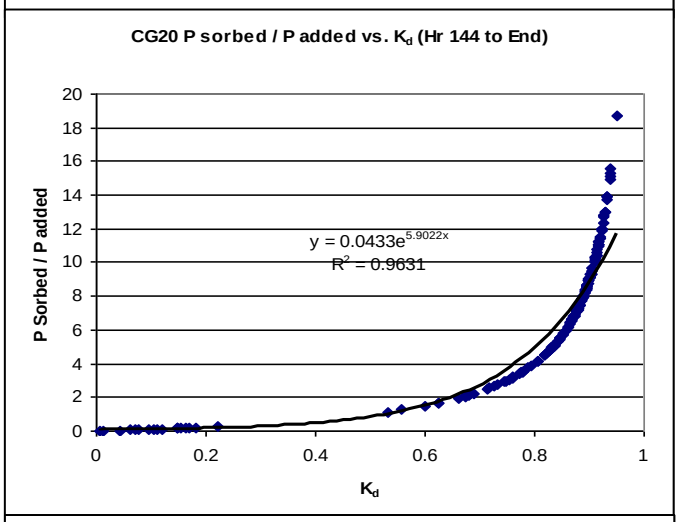
The relative concentration ratio (C/C_0) was plotted against both time and against flow rate. When plotted against time (Figures 20a-f), the CG-type mixtures showed no correlation, while the FGd-type mixtures showed very weak to weak positive correlation. However, when analysis was restricted to the latter part of the study (Figures 21a-f), the FGD-type mixtures have stronger positive correlations between concentration ratio and time. The CG mixture showed a strong correlation as well, but the graph shows a cluster of points rather than any particular trend, so this correlation is suspect (Figure 21a).

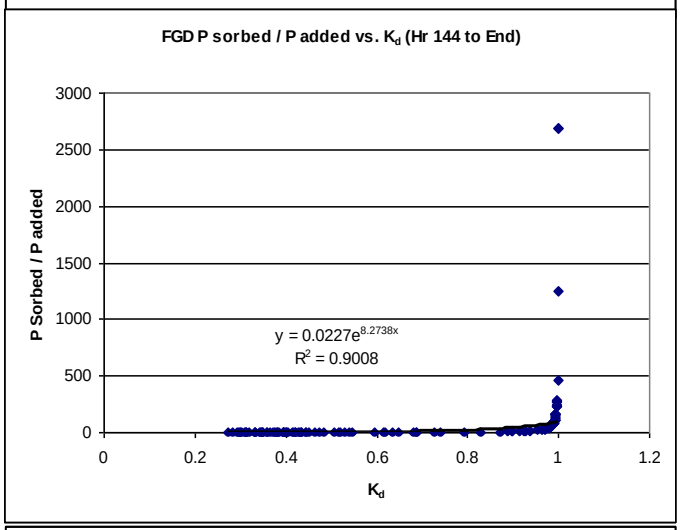


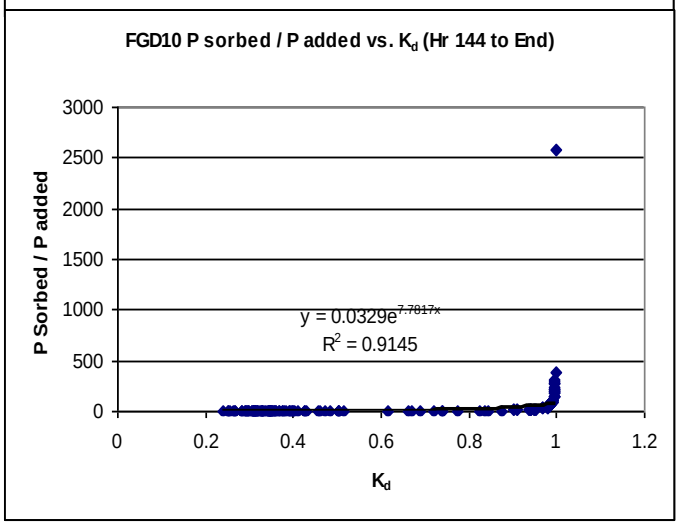
Figures 18a-f: mg P sorbed per mg P added plotted against the partition coefficient for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand).

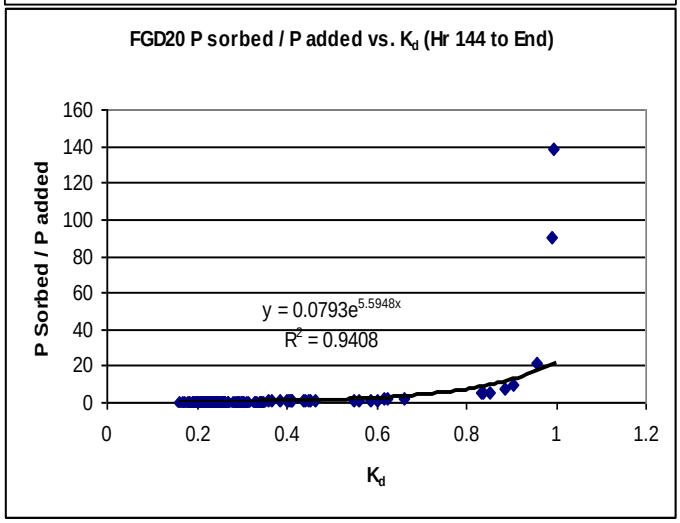




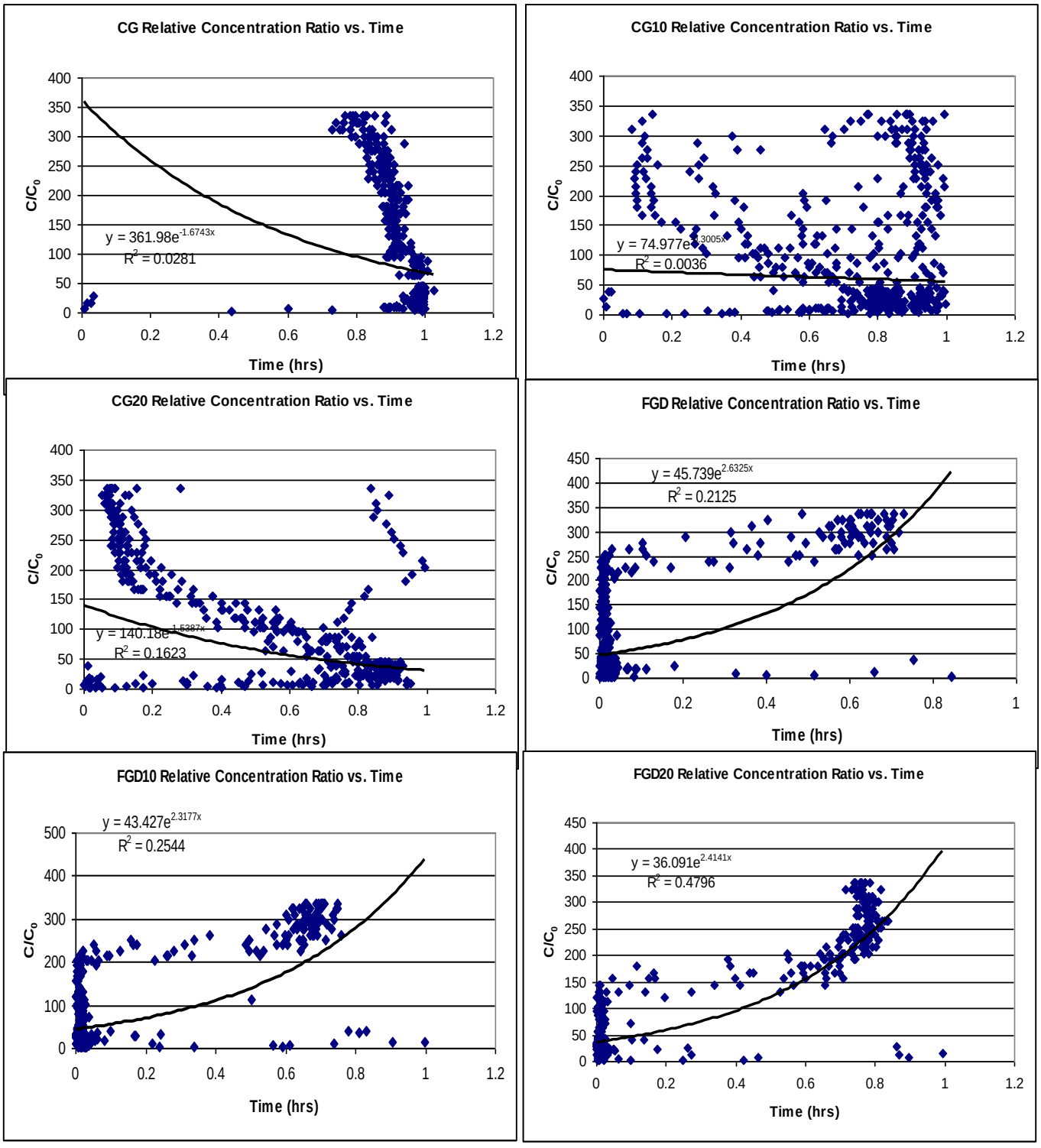




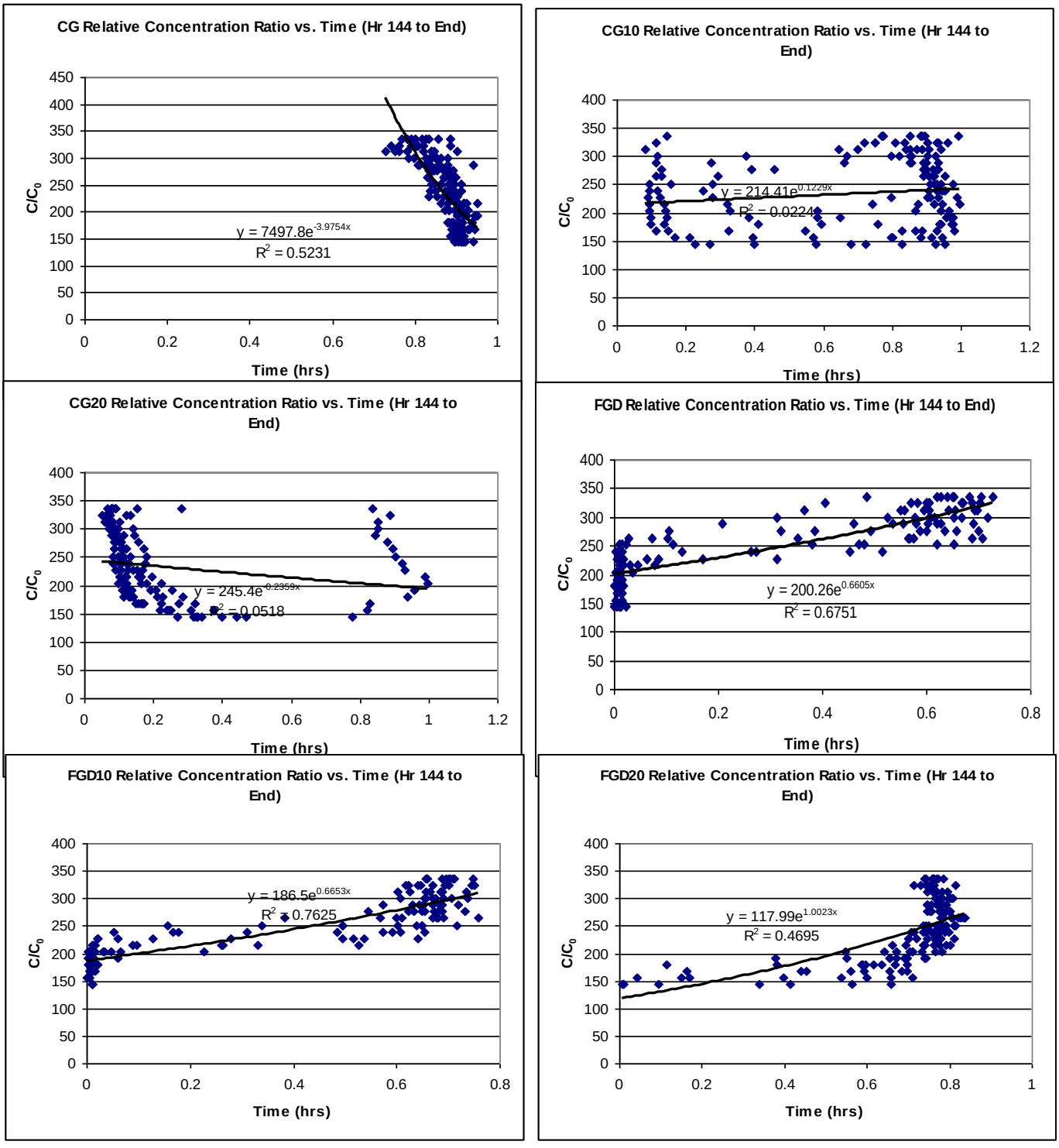




Figures 19a-f: Milligrams P flowing through columns retained by PSM divided by the grams CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against flow rate during the latter part of the study.



Figures 20a-f: relative concentration ratio for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against time.

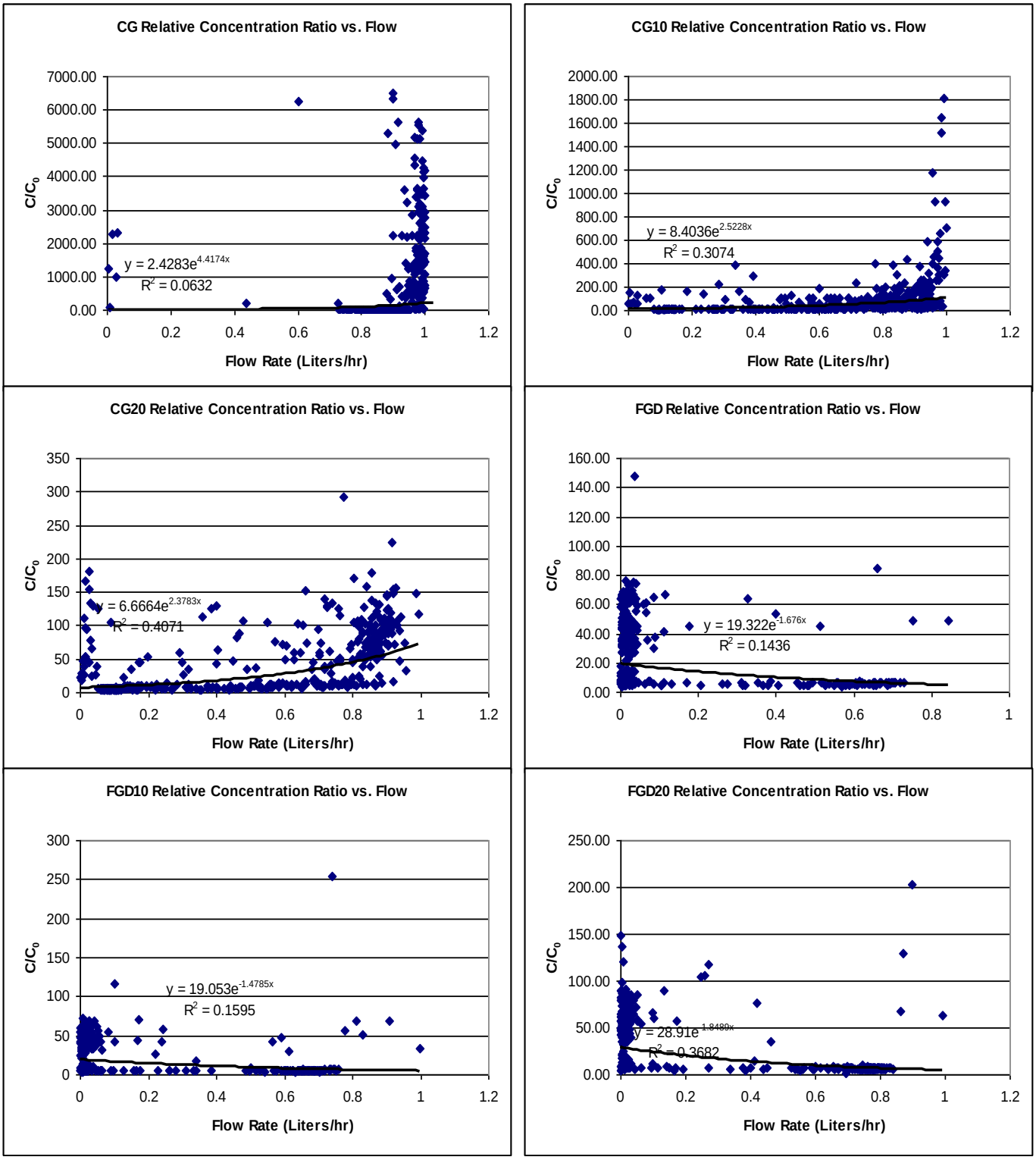


Figures 21a-f: relative concentration ratio for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against time during the latter part of the study.

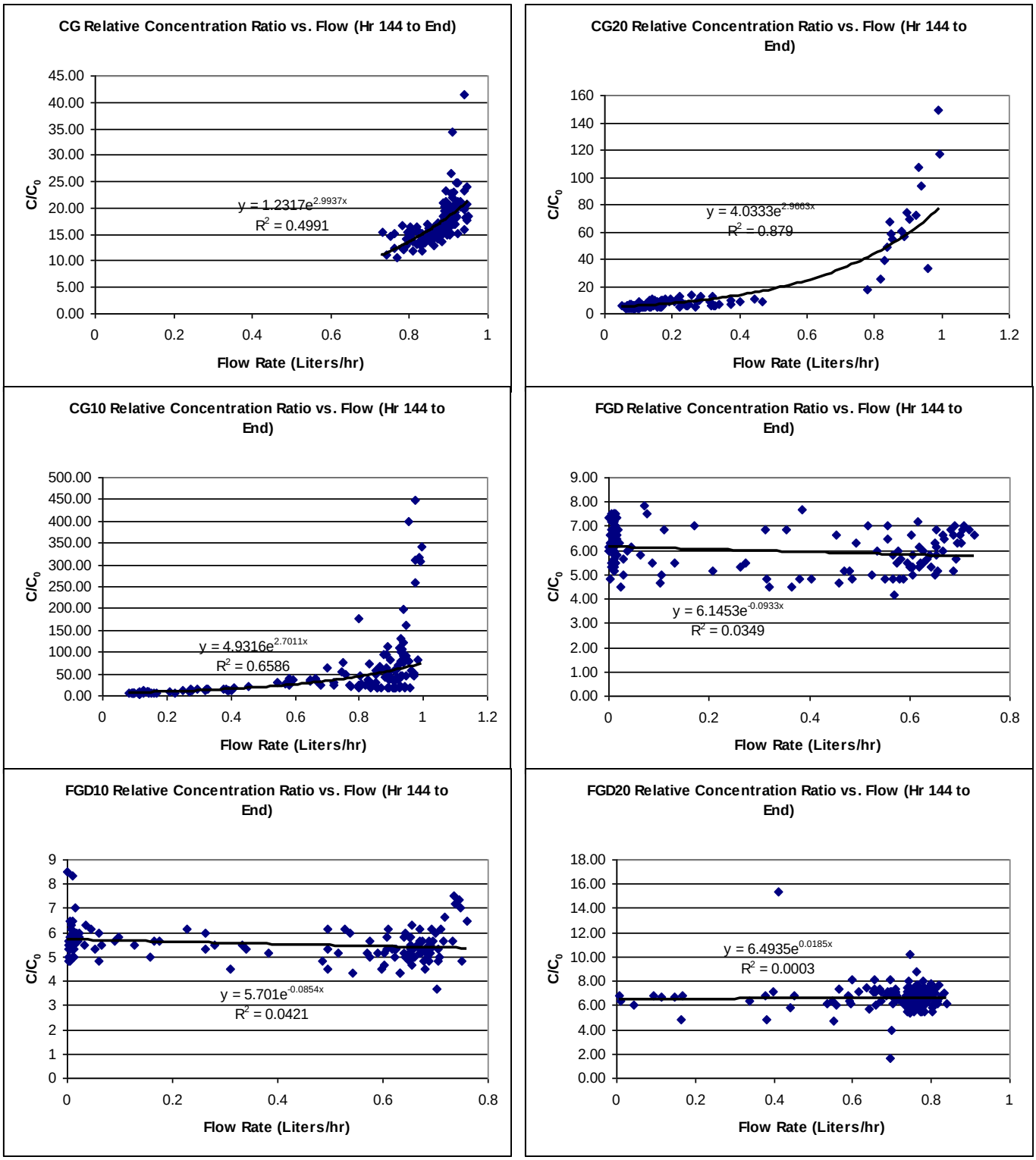
When concentration ratio was plotted against flow rate, there was no correlation for the CG, FGD10 and FGD20 mixtures and weak positive correlations for the CG10 and CG20 mixtures. There was weak negative correlation for the FGD mixture (Figures 22a-f). When analysis was restricted to the latter part of the study (Figures 23a-f), moderate to strong positive correlation was found in the CG, CG10, and CG20 mixtures, while no correlation was found for any of the FGD-type mixtures. This supports the earlier finding that after equilibrium was established, an increase in flow rate decreases the percentage of P sorbed by the CG-type columns.

The cumulative amount of phosphorus sorbed by each mixture was calculated by integrating the total amount retained at each data collection point (Figure 24). However, given the changes in outflow seen in Table 10 as well as high variation in P retention during the first six days of the study, the latter part of the study was again used as an estimate of how the mixtures would perform after having approximated an equilibrium state (Figure 25). A comparison between mixtures shows coarsely ground gypsum as having the least percent P retention, while the CG20, FGD, and FGD10 mixtures had statistically significantly higher P retention than the other mixtures.

The cumulative amount of phosphorus added per mass PSM was then plotted against the cumulative amount of phosphorus sorbed. The CG and CG10 mixtures exhibited no correlation between those values, the FGD and FGD10 exhibited a weak positive correlation, and the CG20 and FGD20 mixtures a strong positive correlation (Figures 26a-f).



Figures 22a-f: relative concentration ratio for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against flow rate.



Figures 23a-f: relative concentration ratio for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against flow rate during the latter part of the study.

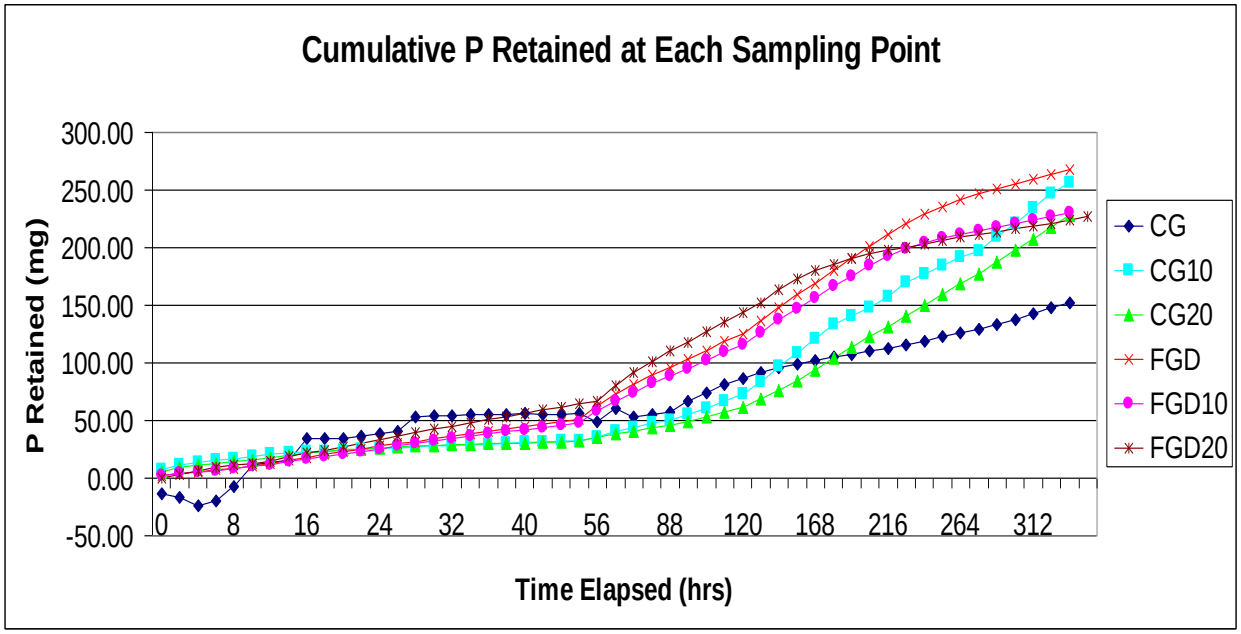


Figure 24: Cumulative phosphorus retention out over the course of the study for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

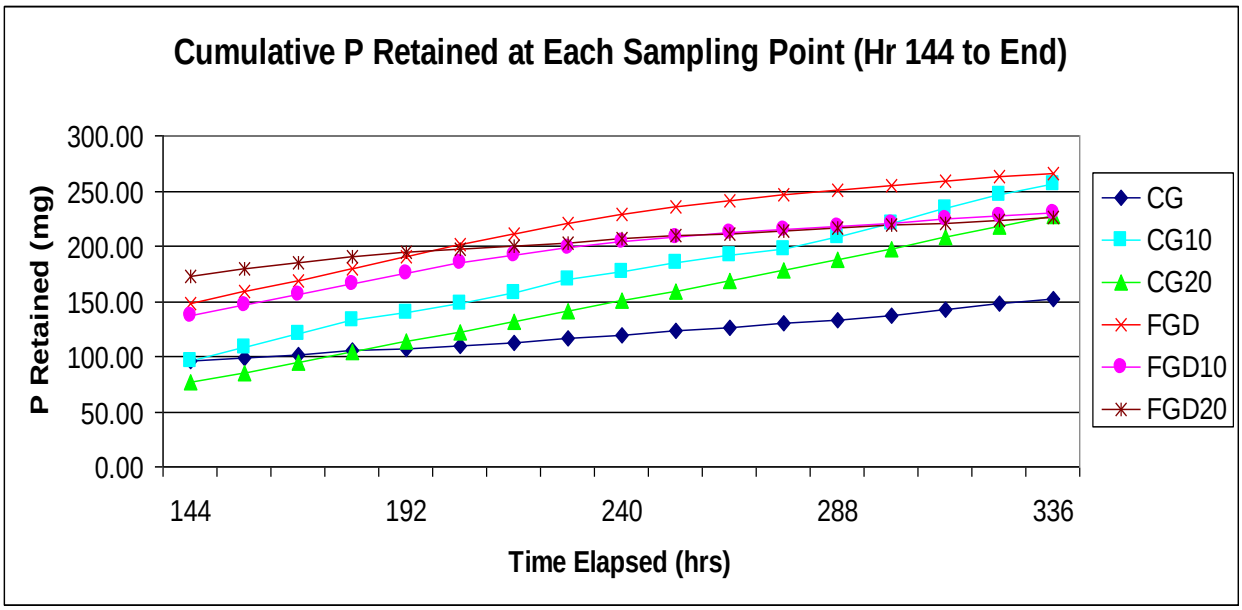
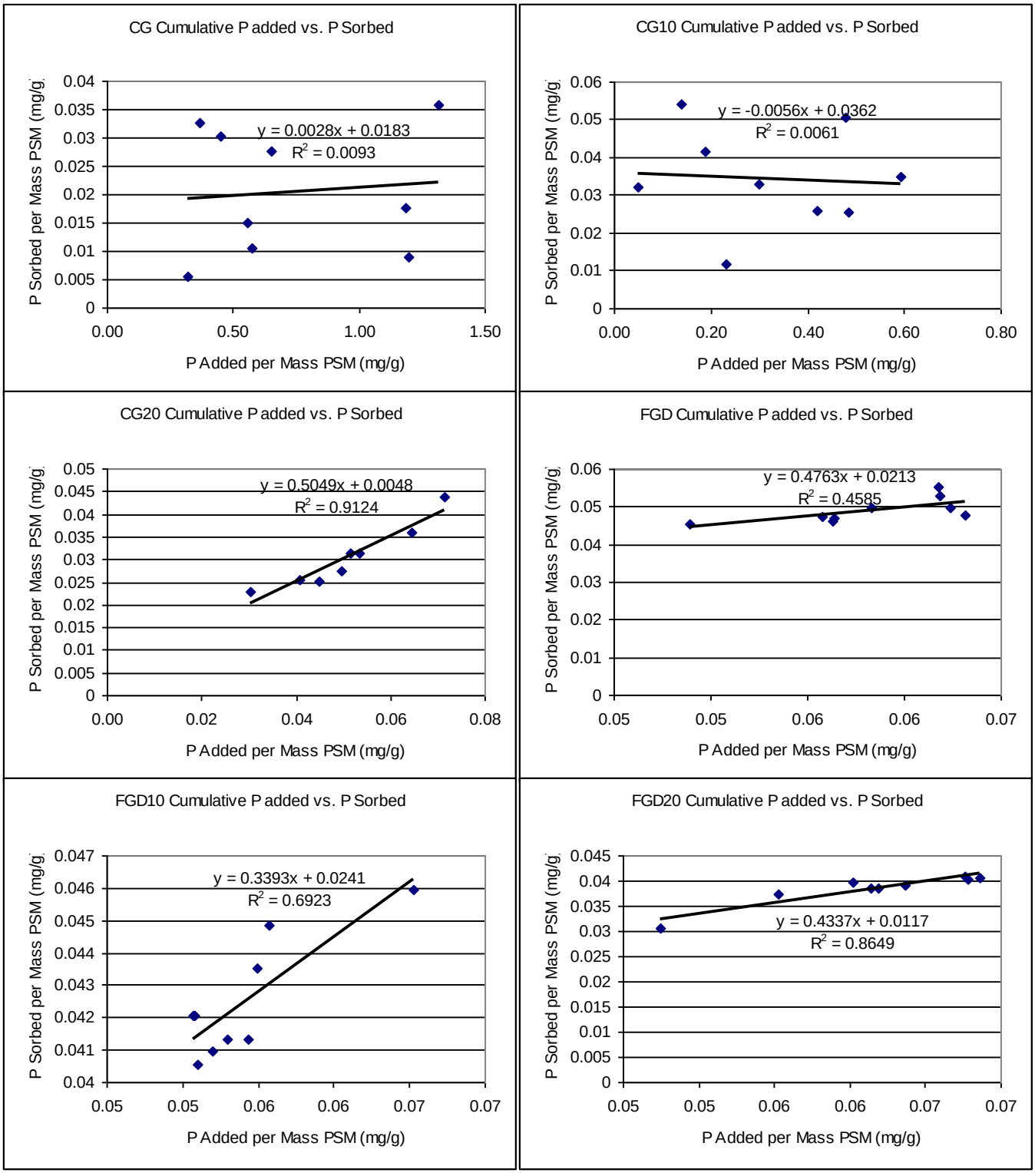


Figure 25: Cumulative phosphorus retention over the latter part of the study for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.



Figures 26a-f: Cumulative phosphorus added per gram PSM for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against cumulative phosphorus sorbed per gram PSM

The amount of phosphorus that exited the columns primarily depended on the volume of P solution flowing through the column and the P retention rate. As the CG and CG10 columns exhibited both higher hydraulic conductivities and lower retention rates than the other treatments, those two mixtures showed much greater effluent P both instantaneously and over the course of the experiment. The FGD-type columns and the CG20 columns did not have higher K values and thus higher P in the effluent until later in the experiment (Figure 8). However, the amount of P leaving those columns was still an order of magnitude lower than the P leaving the CG10 columns.

Because the hydraulic conductivity is predicted to be directly involved in both the amount of P entering the columns and the P retention of the column, the P exiting the column was expected to correlate strongly with the hydraulic conductivity of the columns. These expectations were confirmed by the data (Figure 27).

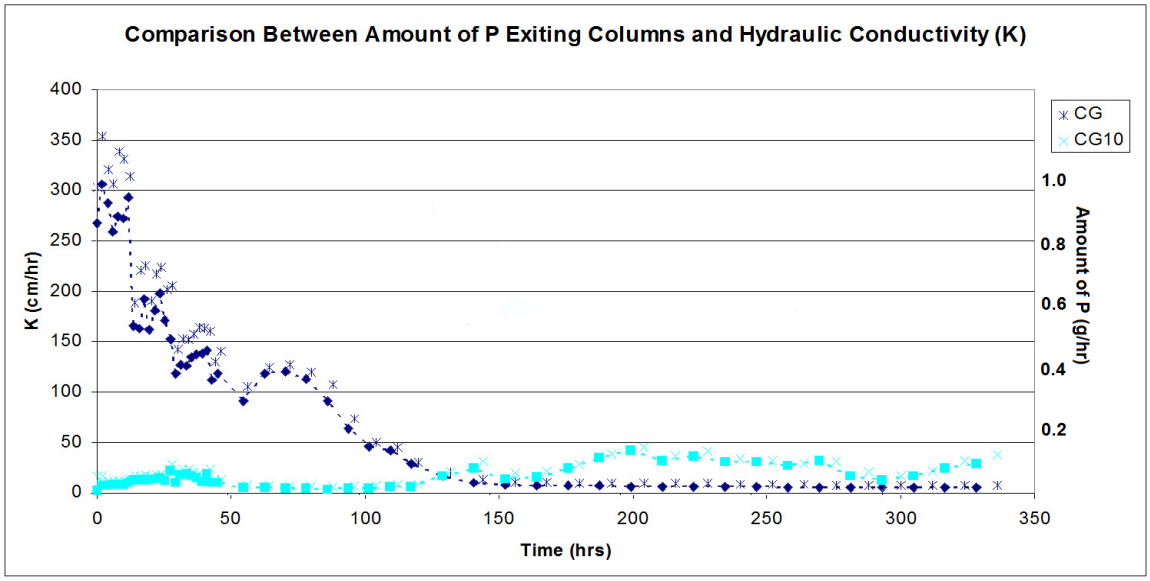


Figure 27: Rate of P exiting the columns varying as a function of time elapsed (solid points) overlaying the change in K values as time elapsed (crosses). The left Y axis scale corresponds to hydraulic conductivity while the right Y axis scale corresponds to the rate at which P exited the columns.

When trying to apply the results to a filter in the field, the amount of P exiting the columns would have to be compared with the amount of water expected to go through the filter.

While the FGD-type columns do not have large values for this experiment, the design fed only as much water into the column as necessary to maintain a constant head. In a case of large amounts of water such as the CG and CG-10 columns experienced, this would result in overflow and the P load in the ditch water would have to be added to the P found to be exiting the filter, as has been seen in ditch filters using FGD gypsum (Bryant et al, 2012).

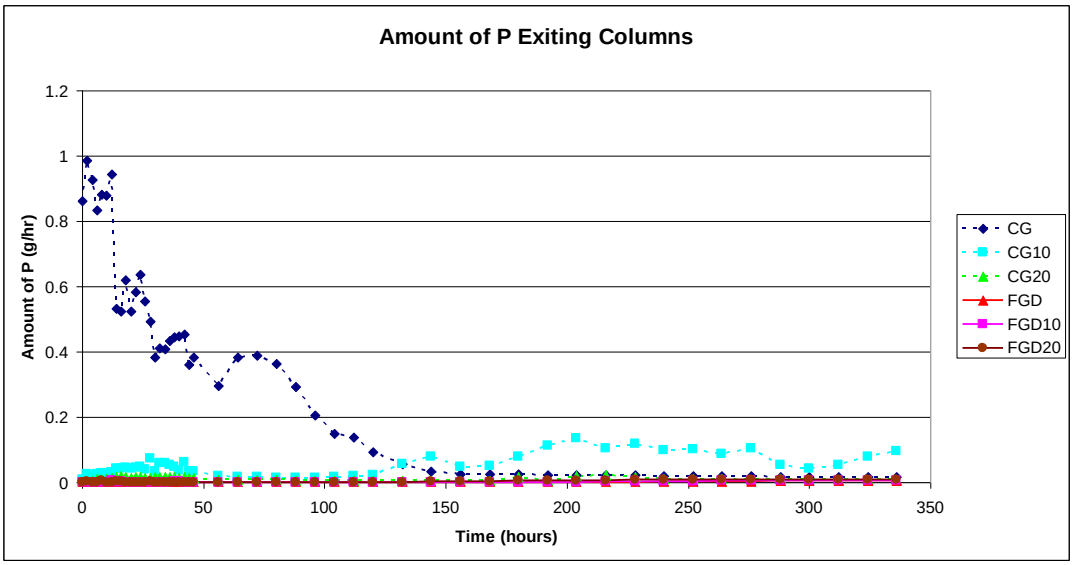


Figure 28: Averaged rate of phosphorus (P) that exited the columns over the course of the study for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

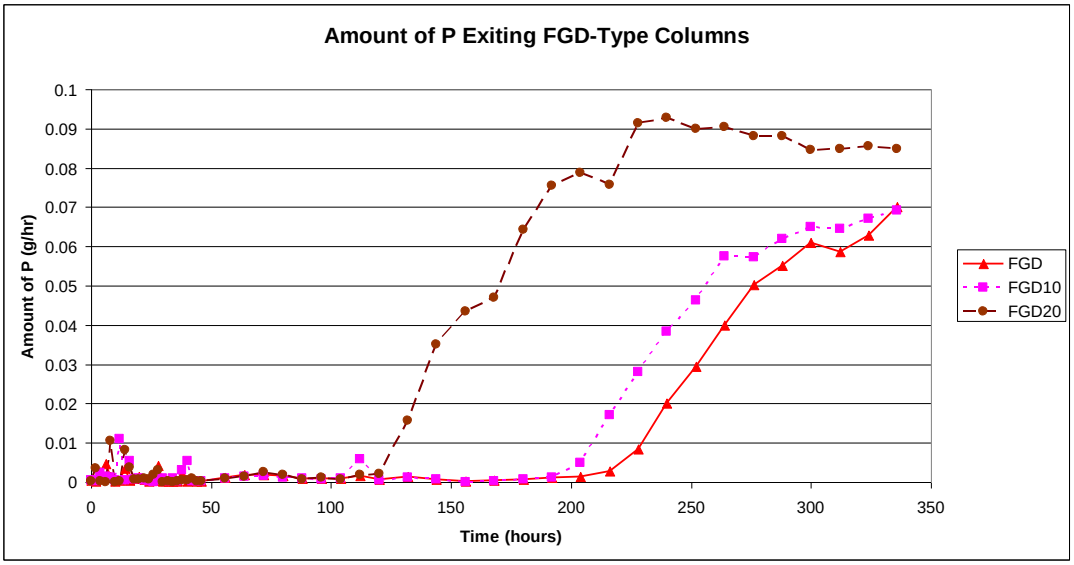


Figure 29: Averaged rate of P exiting the FGD-type columns over the course of the study. Note the difference in the y-axis scale between Figures 18 and 19.

The average total amount of phosphorus that passed through each column was estimated for each mixture (Figures 30-32). In this case, greater amounts of flowthrough naturally led to a greater amount of P exiting the column. However, it must be remembered that initial field tests of gypsum ditch filters resulting in stormwater overflowing the filter and not passing through the gypsum layer at all. Although the purpose of this study was ideally to determine a mixture that has a reasonably high hydraulic conductivity while maintaining a near-zero amount of P exiting the column, it is again apparent in these results that there exists a trade-off between maintaining proper flow rates and allowing some P to exit the column. However, there is evidence that somewhat higher flow rates can still result in extremely low levels of P in the effluent, as in the case of the CG20, FGD, and FGD10 mixtures (Figures 31 and 32) .

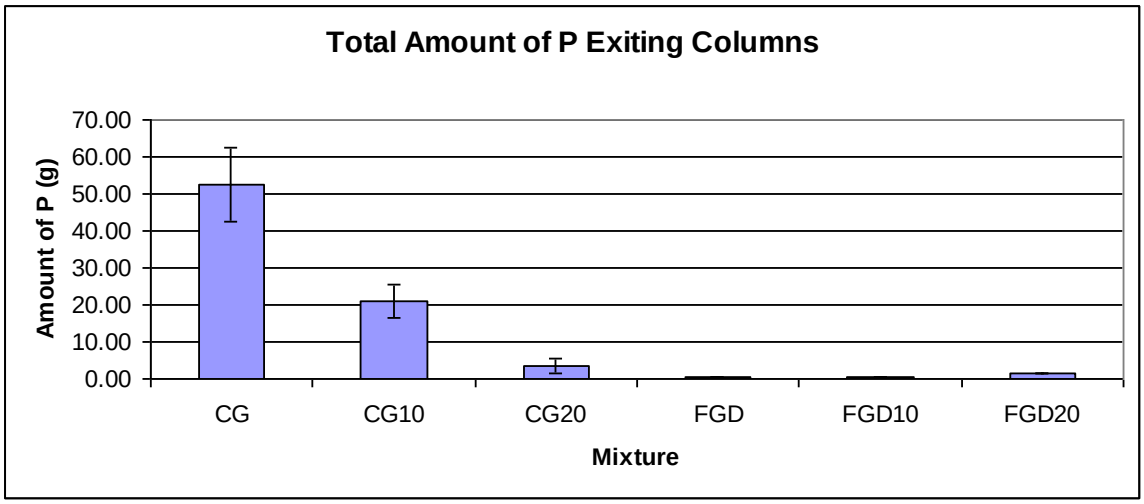


Figure 30: Estimated total amount of P that exited the columns For the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

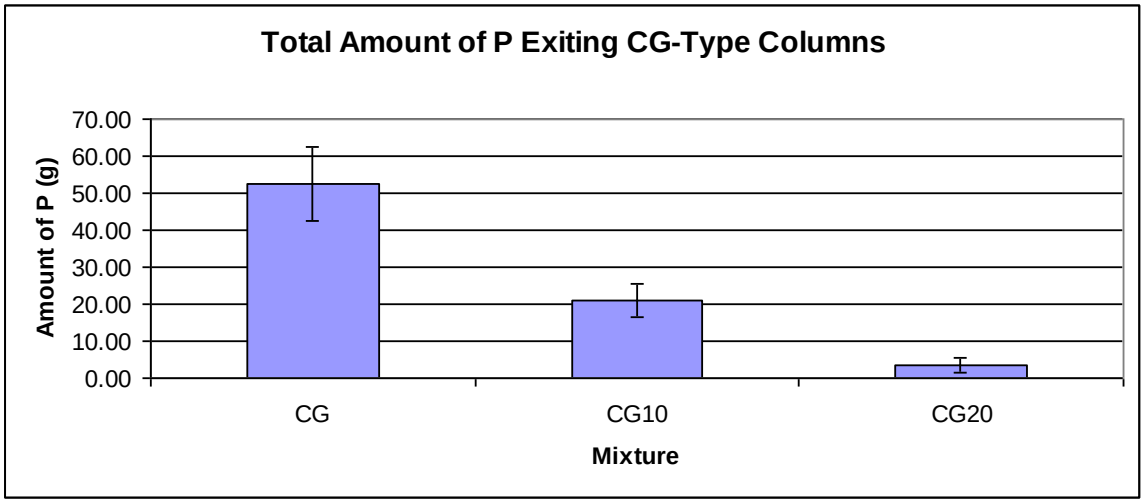


Figure 31: Average total amount of P that exited the CG-type columns.

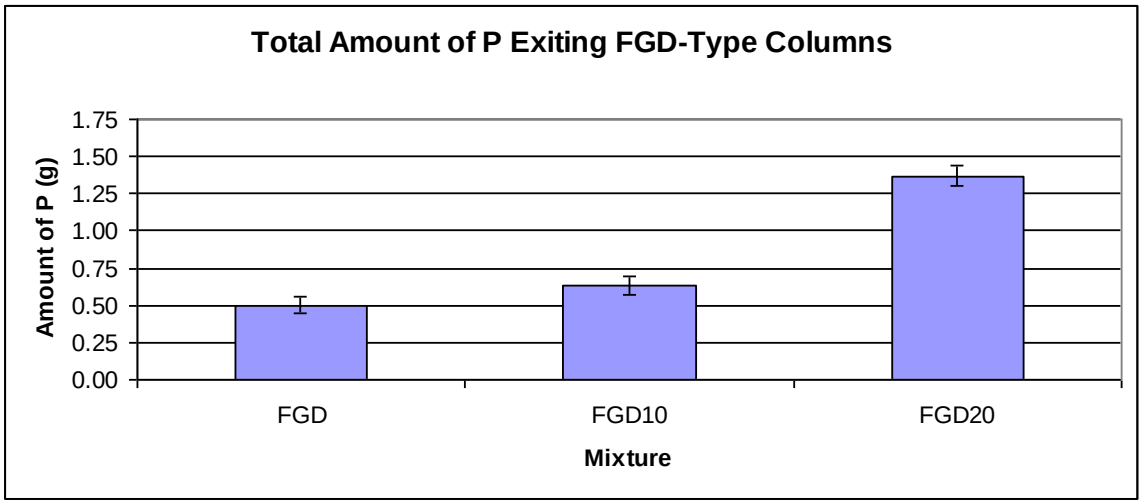


Figure 32: Average total amount of P that exited the FGD-type columns. By comparison, the estimated total for CG20 was 3.51 ± 2.02.

The amount of total phosphorus removed was estimated based on multiplying the percent of P retained by the instantaneous flow-through and then summing for the duration of the study (Figure 33). When looking at the total phosphorus retained by the columns over the duration of this study, it was found that the mixtures did not show a significant difference with the exception of the pure CG treatment, which was significantly lower than the other mixtures. Pressure head was not found to have a significant effect because of differences in final column heights and the inherent variability of the saturated hydraulic conductivity. There were technical limitations on

which pressure heads could be used, and it is possible that if the system were redesigned to allow a greater range of pressure heads then significant differences may have been detected.

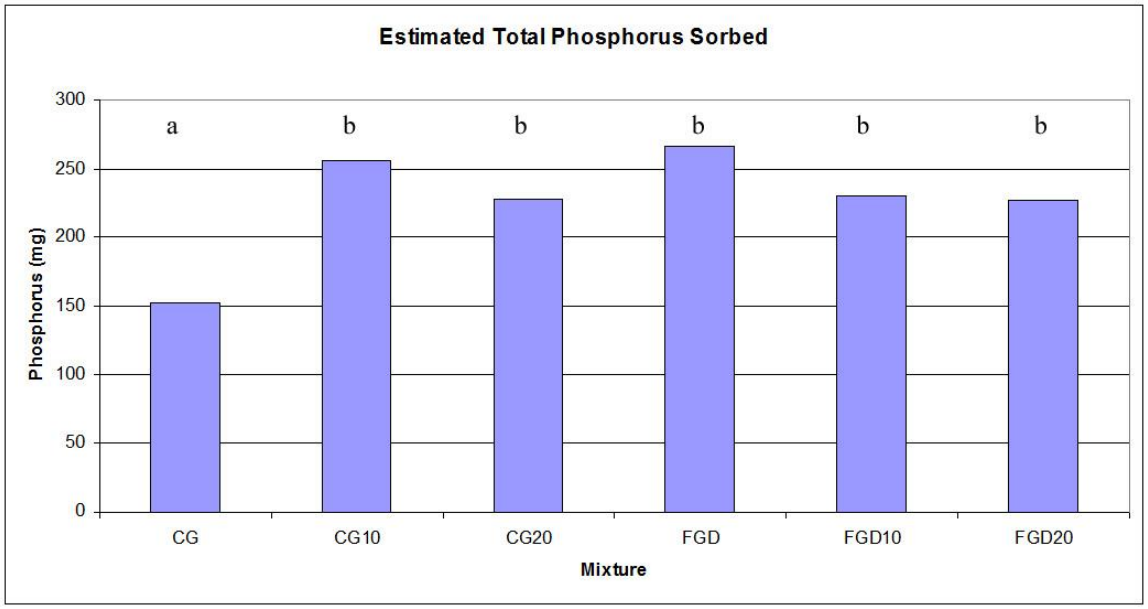


Figure 33: Average total quantity of phosphorus removed from solution for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures. Different letters indicate statistical significance at the $P<0.05$ level using Tukey's Means Comparison Test.

These measurements displayed no significant differences between any of the mixtures except the unaltered coarse gypsum in terms of the total amount of phosphorus removed from the solution during the course of the study. Unaltered coarse gypsum removed significantly less phosphorus than the other mixtures, most probably due to extremely high hydraulic conductivities during the early part of the study which had the effect of reducing the retention time below the time necessary for gypsum to precipitate out the phosphorus in solution. However, this leaves the other five mixtures still under consideration. These results can then be compared with the hydraulic data to select the proper set of characteristics for a given situation. Where a filter PSM is necessary, where there is high base flow, and also frequent, strong precipitation events, the mixture that would likely allow the most flow through the column while

still maintaining a fairly high percentage of P removal would be the CG10 mixture. However, the CG10 mixture has a lower hourly percentage of P removal than the CG20 mixture and the FGD-type mixtures. The two mixtures with the highest P removal percentage by the end of the study were CG20 and the unaltered FGD, with the CG20 mixture having slightly higher hydraulic conductivity values. Therefore, in a filter situation that features low base flow and smaller storm surges, it might be better to use the greater P sorption capacity of the CG20 or FGD mixtures. However, large storm surges could still result in a good deal of filter overflow even with the addition of 10-20% of sand to the FGD gypsum.

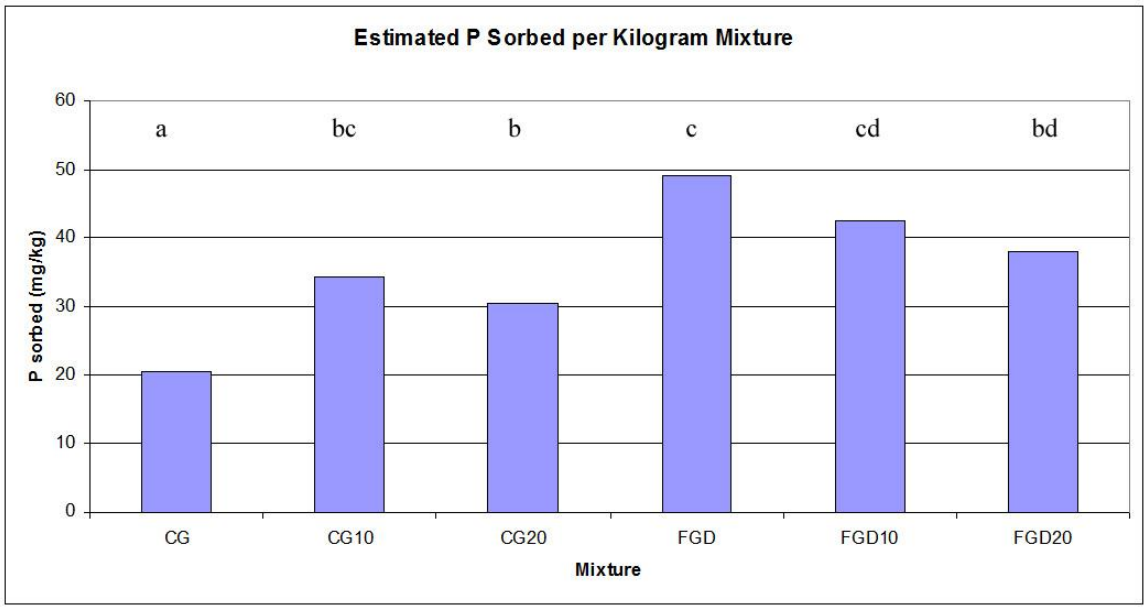


Figure 34: Average amount of phosphorus removed from solution divided by the mass of the column material for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

This total phosphorus value was divided by the kilograms of mixture added, as that value would be used to estimate the efficacy of large-scale drainage ditch filters. FGD gypsum is significantly less dense than the coarse gypsum used (0.94 g/cm^3 vs. 1.71 g/cm^3), and so those columns that were comprised of a FGD-type mixture required significantly less material in terms of mass than the CG-type columns. The FGD-type mixtures showed greater P sorption per

kilogram material than the CG and the CG20 mixtures, although they could not be statistically separated from each other or the CG10 mixture (Figure 34). This result could have an effect on final selection of a drainage ditch filter material outside of consideration of P sorption and hydraulic properties, as a large portion of the cost of ditch filter installation is transport of the PSM material.

The repeated sampling undertaken during the column study revealed there was a good deal of mixture-dependent variation in the amount of leachate exiting the columns over the course of the study. The broad trends are that the flow rate of the CG mixture decreased while all the other columns exhibited increased flow rates, notably the CG10 columns (Figure 8). The other four mixtures did not exhibit significant differences from each other, and the addition of sand was not found to have an effect on the flow rates of FGD gypsum at the concentrations of sand used (Figures 9, 37).

Over the limited course of this study the CG mixture showed significantly more total flow-through than the other mixtures (Figure 35). However, near the end of the study the CG mixture exhibited drastically reduced flow rates, while the CG10 mixture exhibited increased flow rates, surpassing the CG mixture by hour 132. If these trends were extrapolated over a greater length of time (for instance, the lifespan of a ditch filter), the CG10 mixture would allow the greatest total leachate through the columns (Figure 36). It should also be noted that when the latter part of the experiment (hour 144 to the end of the experiment at hour 324) is compared to the earlier part, every mixture besides the pure CG mixture showed an increase in flow rates (Figures 35, 36).

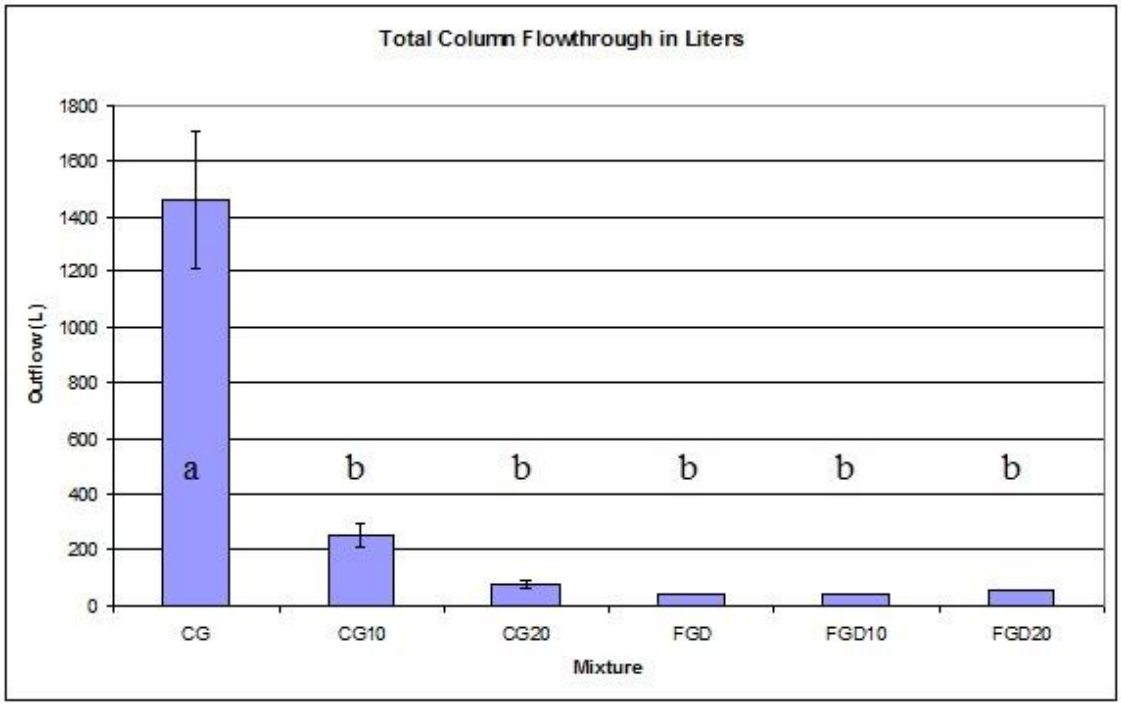


Figure 35: Estimated total volume of solution that passed through columns. Different letters indicate statistical significant differences in means comparison using the Tukey test at the P<0.05 level.

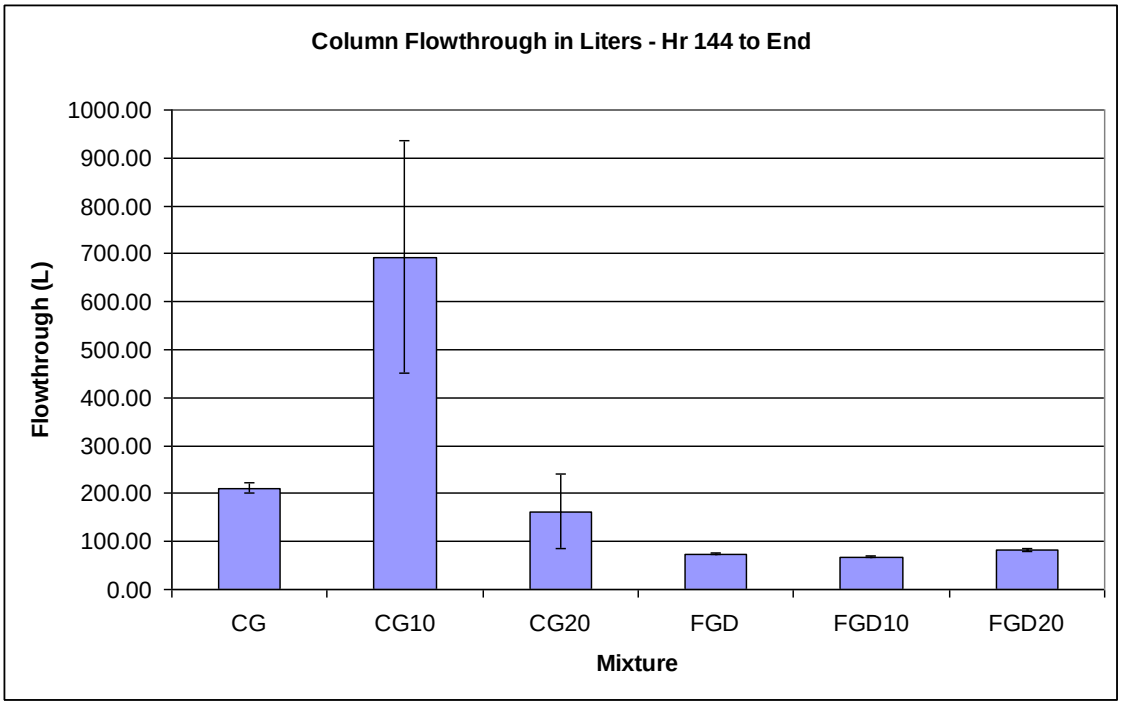


Figure 36: Total volume of solution (outflow) that exited the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) columns following 144 hours of constant flow.

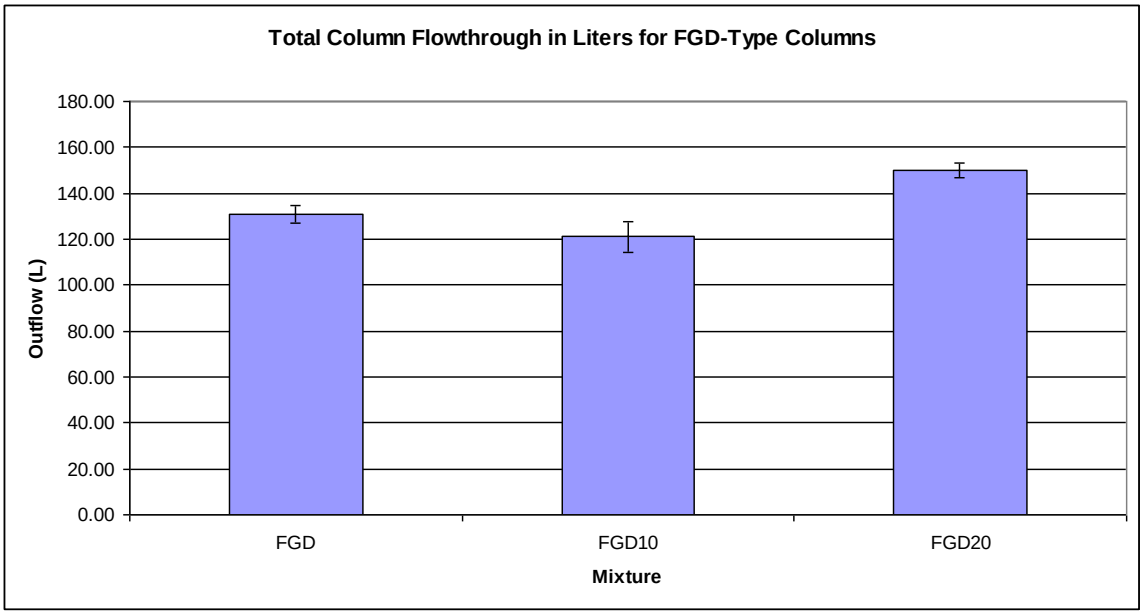


Figure 37: Total volume of solution (outflow) that exited the FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) columns.

Distribution of P Sorbed Within Columns

The distribution of sorbed P within the columns after the flow measurements were completed is correlated to the hydraulic conductivity of the columns. P traveled farthest before uptake in the columns that had greater amounts of water movement through the column. The FGD-type columns contained far more sorbed P at the surface (the material within the top centimeter of the column) than the CG-type columns, but that difference quickly diminished until becoming insignificant at 15 cm below the surface (Figure 38). The CG-type columns had a greater amount of P located at 15 cm below the surface, although this difference was not significant. The high concentration of P at the surface of the FGD-type columns correlates with the presence of suspected iron sulfides at the surface of those columns. It is possible that as the matrix of this new substance formed, it trapped phosphate within the crystal structure without directly adsorbing it.

Pressure head was found to have a significant effect at the surface - the columns under 12 cm head had higher amounts of P at the column surface. Pressure head was not found to be a significant factor at any other depth (Figure 39). Again, the mixture used in the columns also had the greatest effect on P deposition at the surface of the columns.

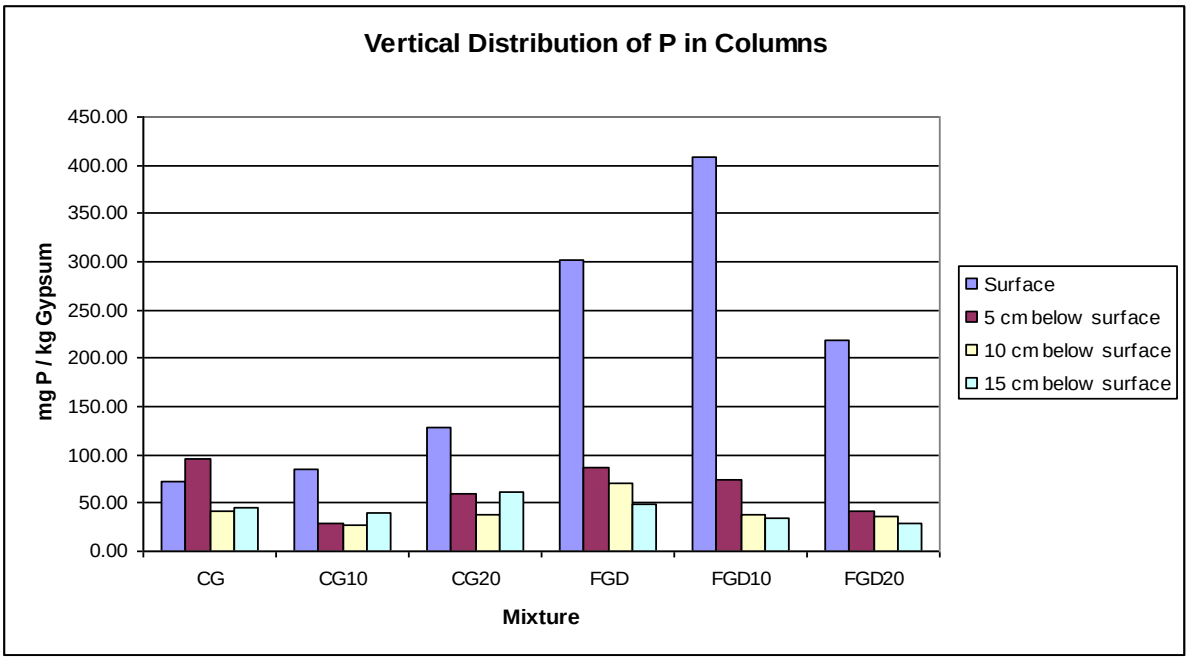


Figure 38: The average amount of P found at different depths within the column for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures..

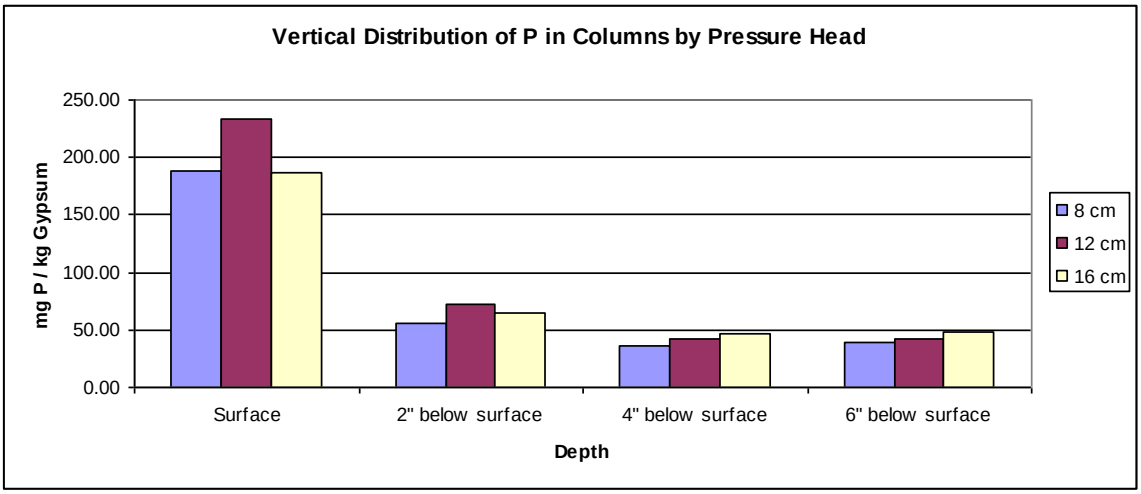


Figure 39: The vertical distribution of phosphorus (P) within the columns. Pressure head only had a significant effect on P presence at the surface of the column.

Bromide Tracer Results

Bromide was used as a convective tracer to model solute transport through the columns. It is used regularly with soils because in most cases soil does not interact with bromide. However in the gypsum columns used the results indicate some type of interaction between the bromide and the column matrix. It is possible the formation of the brittle, porous material at the top of the column had an effect on the bromide tracer. This possibility was tested by a nitric acid extraction on this material and also through measurements on material 1 cm below the line of change. The extracted solutions were tested for bromide with an ion-selective electrode, but results of this test did not show elevated levels of bromide within the gypsum matrix.

The bromide tracer results generally indicated complete leaching of the tracer occurred faster than expected. While there was more bromide leaching entirely through the CG-type columns than the FGD-type columns during the first two hours of the experiment, during the second sampling period there was more bromide exiting the FGD-type columns than even the CG-type columns. By the fourth sampling period (8 hours of leaching), there were no longer any significant amounts of bromide leaching from any columns. These results were unexpected, as at that time the pure CG columns had leached an average of 19 pore volumes, but all other mixtures had leached less than one pore volume. It is generally thought that not until after eight pore volumes of leachate has passed through a column the total quantity of a non-reactive tracer would have exited the column. Pressure head was not found to have a significant effect, although the interaction between pressure head and mixture was significant during the first sampling period. This significant interaction is because the CG columns under 8 cm of pressure head leached far less bromide than those under 12 and 16 cm of head (Figure 40). Given the unreliable nature of these results, it is recommended that any future bromide tracer studies be instead done with liquid chromatography.

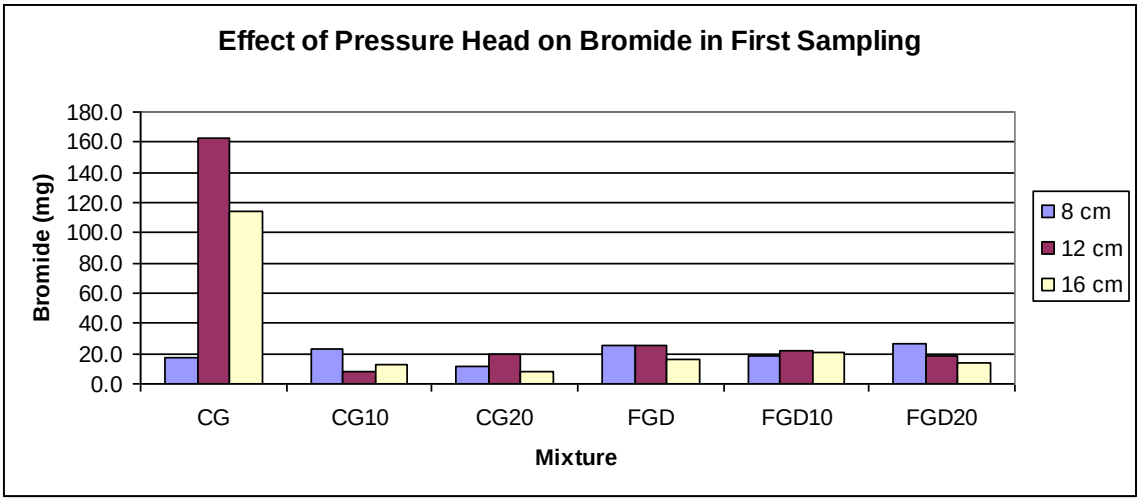


Figure 40: The average quantity of bromide that exited the columns for the different pressure heads during the first sampling for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

As has already been seen with the iron sulfide pore linings, there is evidence that preferential flow is present in these columns, which would explain this discrepancy. The quantity of bromide exiting the columns was calculated by multiplying the Br concentration of the samples by the amount of flowthrough during the corresponding sampling period. The resulting range of total bromide exiting the columns was between 13 and 98 mg of bromide, and does not correspond well to the 10 mg of bromide that were added to each column. As is seen in Figure 39, five of the mixtures leached an estimated amount of bromide relatively close to the expected 10 mg, and only the CG mixture was very far from 10 mg. That particular mixture had an extremely high flow rate, especially in the first few sampling periods, and thus had extremely large volumes that, when multiplied by the concentration determined by a bromide electrode, would greatly exacerbate any possible errors in bromide concentration measurement (Figures 41-44).

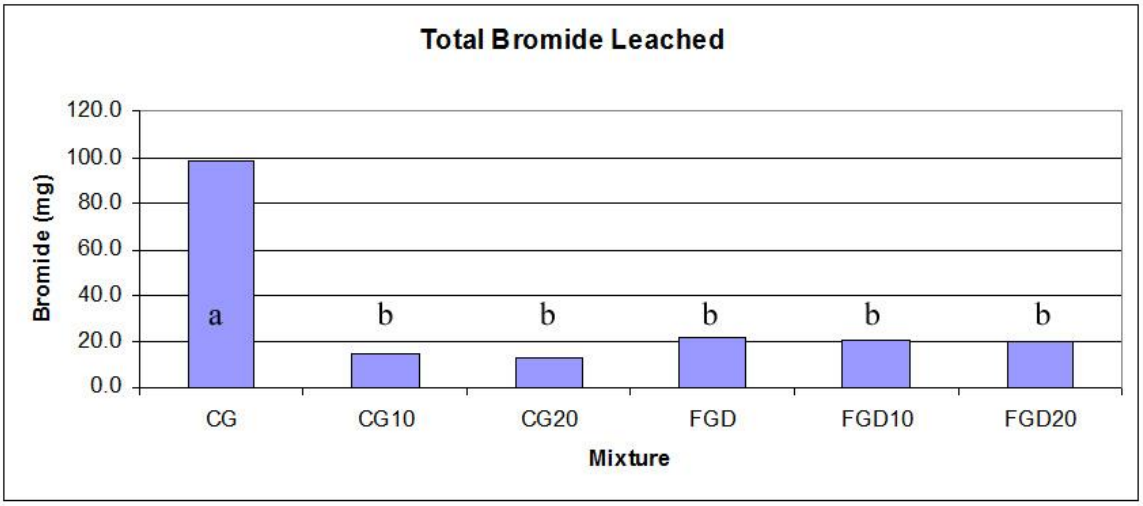


Figure 41: The total quantity of bromide leached from the columns for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

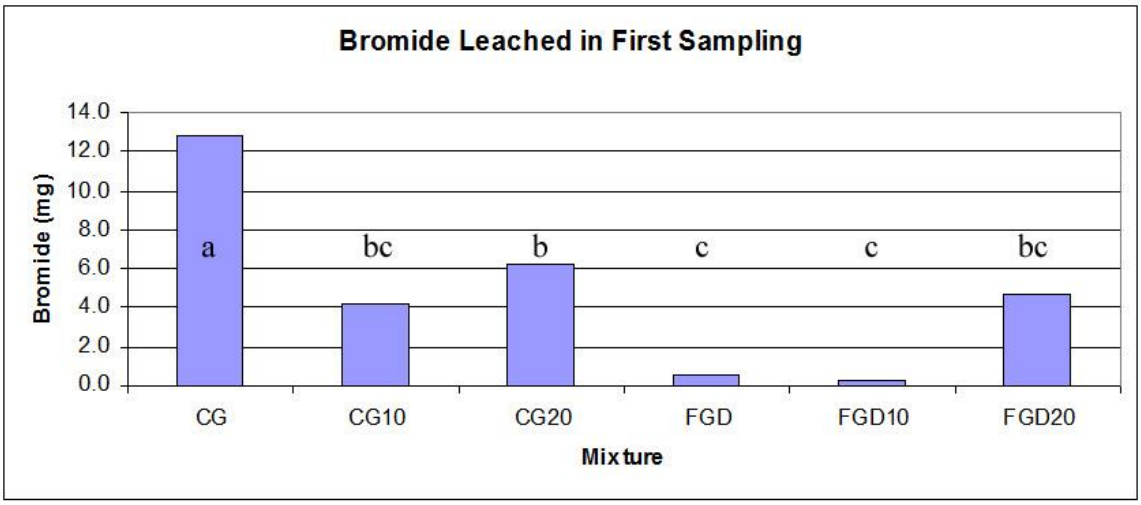


Figure 42: The quantity of bromide leached during the first two hours for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures..

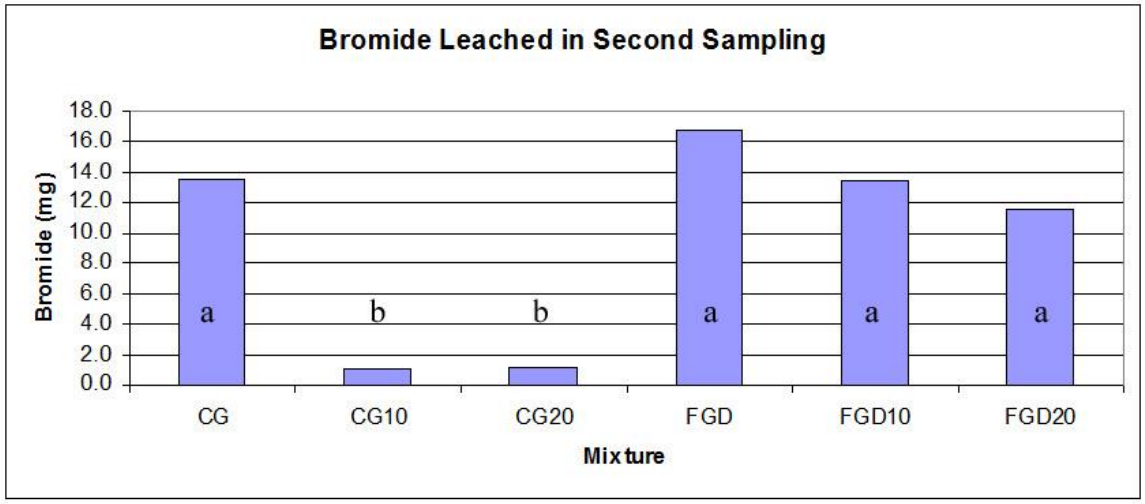


Figure 43: The quantities of bromide leached during hours 2-4 for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures..

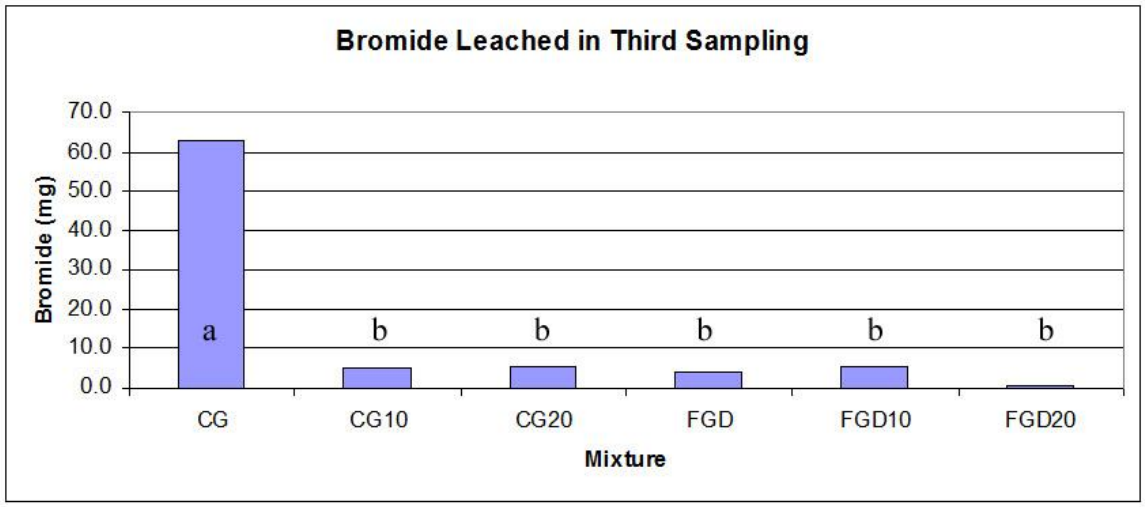


Figure 44: The quantity of bromide leached during hours 4-6 for the CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures.

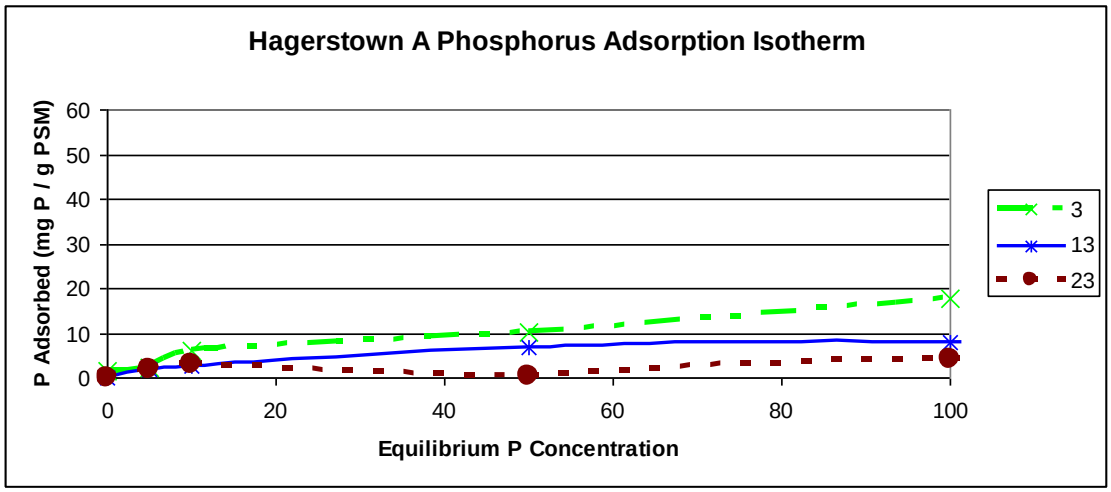
Suggestions for Further Research

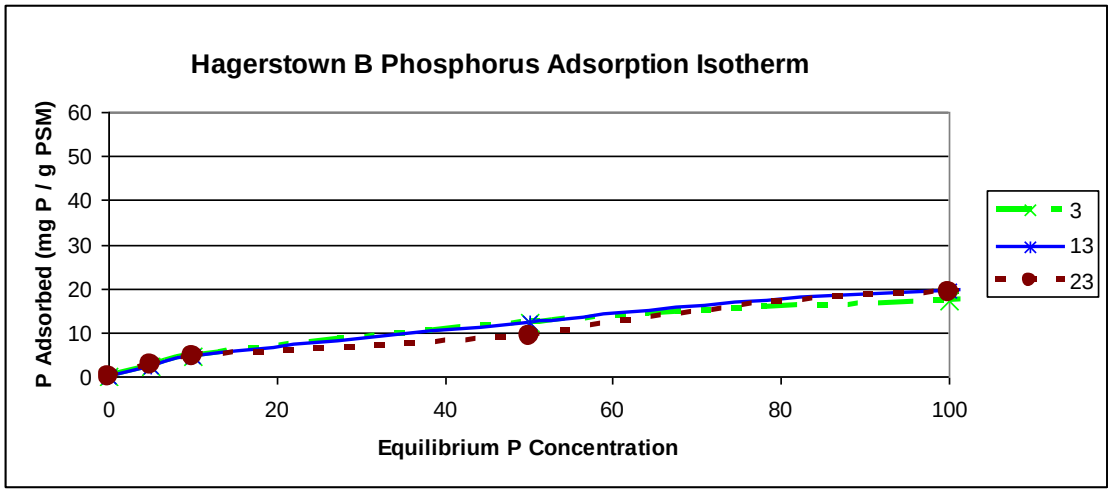
As the 24-hour period of shaking in the isotherm study may have been too long to effectively capture kinetic differences in these PSMs, a graduated isotherm study using different periods of time could be beneficial. Shaking times such as 30 minutes, 1 hour, and 4 hours could illuminate temperature-related kinetic differences.

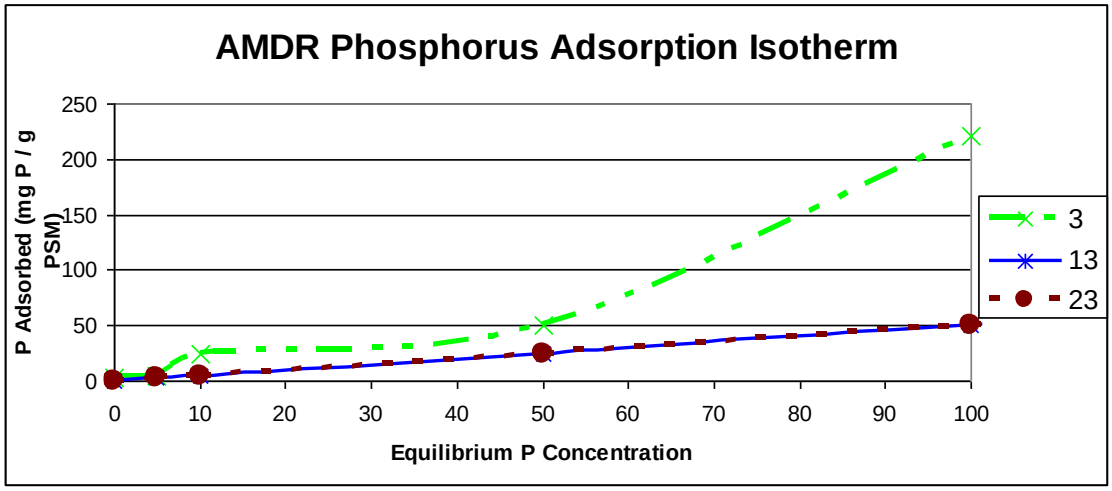
Using a greater range in the different pressure heads could elucidate differences in flow rate and P sorption due to hydraulic head. Also, an examination of the effect of greater percentages of sand in the FGD mixtures could be useful if the emerging trend of greater hydraulic conductivity with greater amounts of sand develops into significant differences, especially as thus far greater amounts of sand had not significantly diminished P sorption. The possibility of mixing FGD gypsum with another material (such as sand) as a means of interfering with surface sealing could be investigated.

Appendices

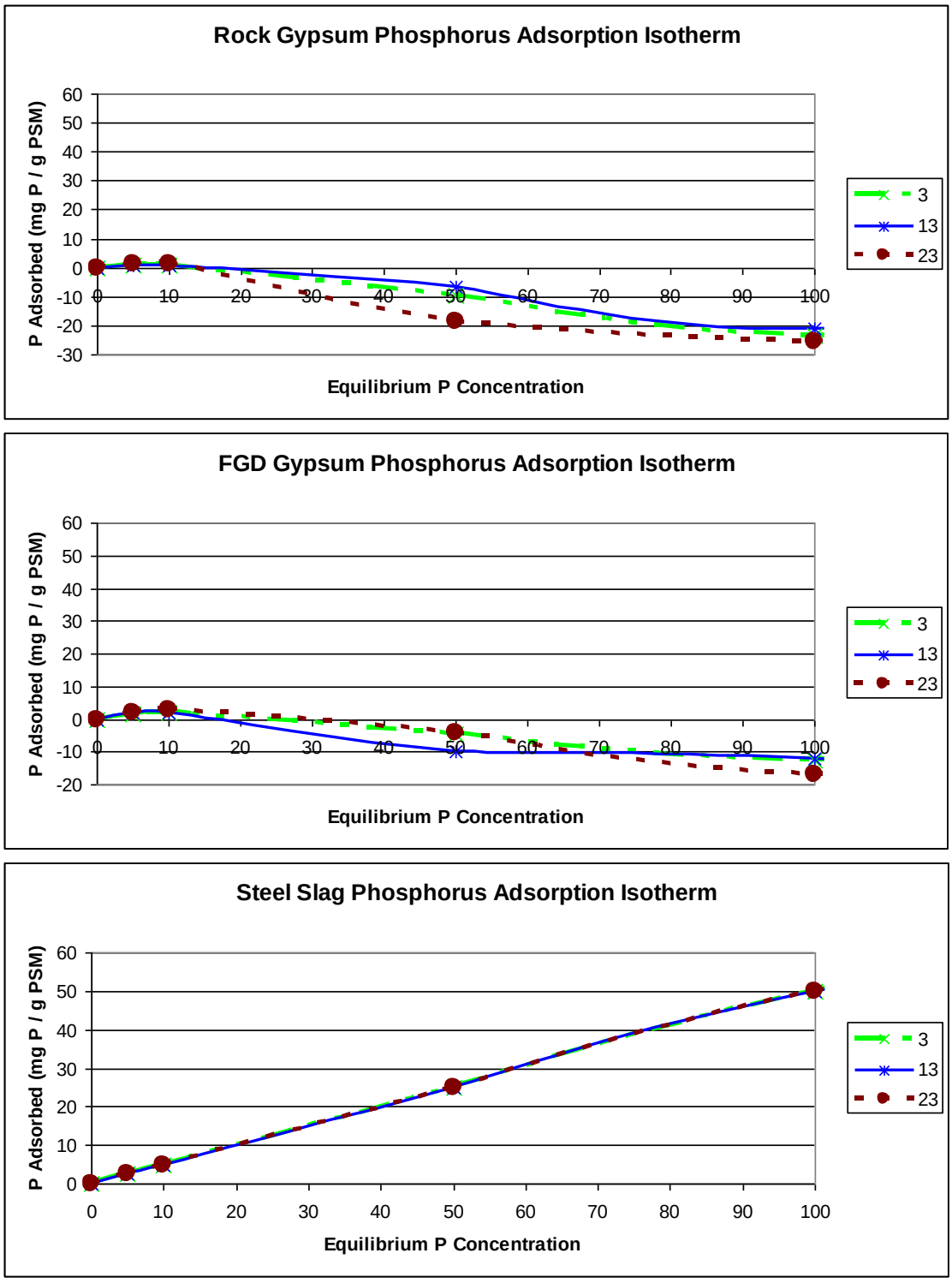
Appendix A: Isotherm data for each PSM as a function of temperature.





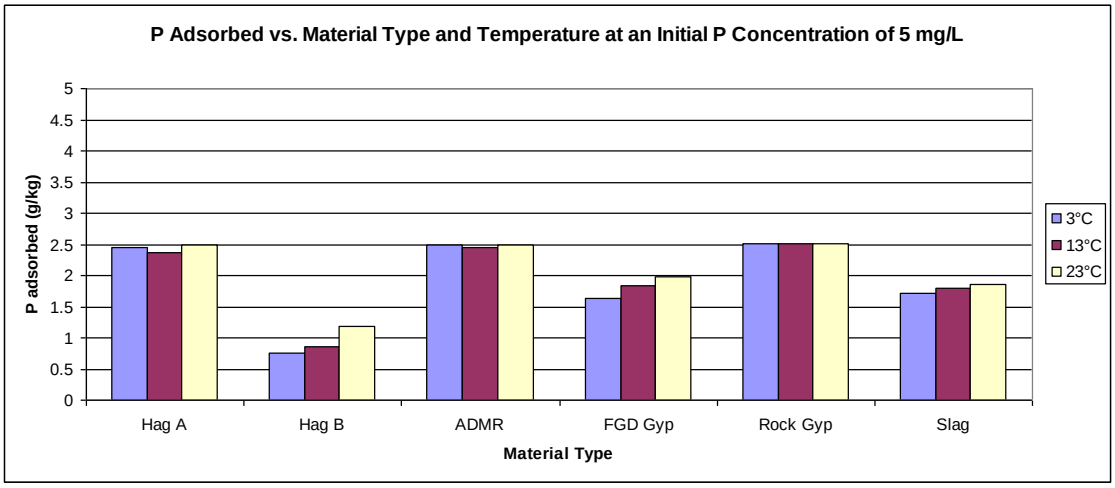


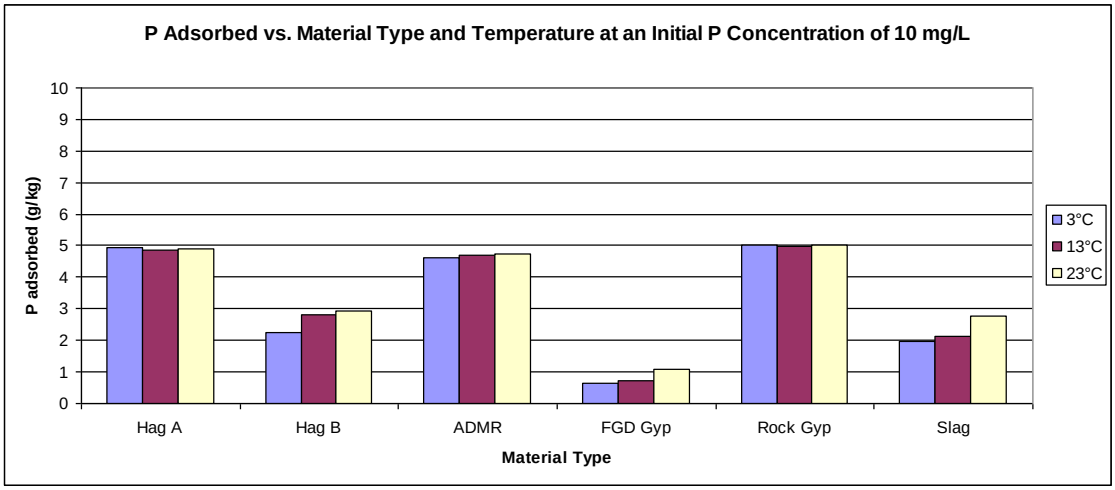
Figures 45a-c: Isotherms showing P adsorbed vs. equilibrium P concentration for the Hagerstown A and B soil horizons and the ADMR (Acid Mine Residuals) PSMs.

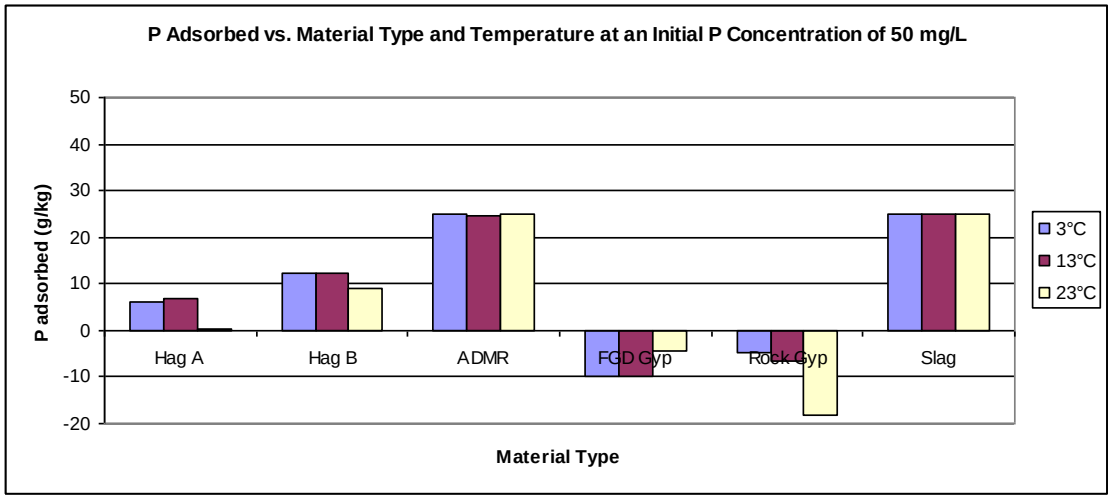


Figures 45d-f: Isotherms showing P adsorbed vs. equilibrium P concentration for the natural rock gypsum, FGD (flue-gas derived) gypsum, and steel slag PSMs.

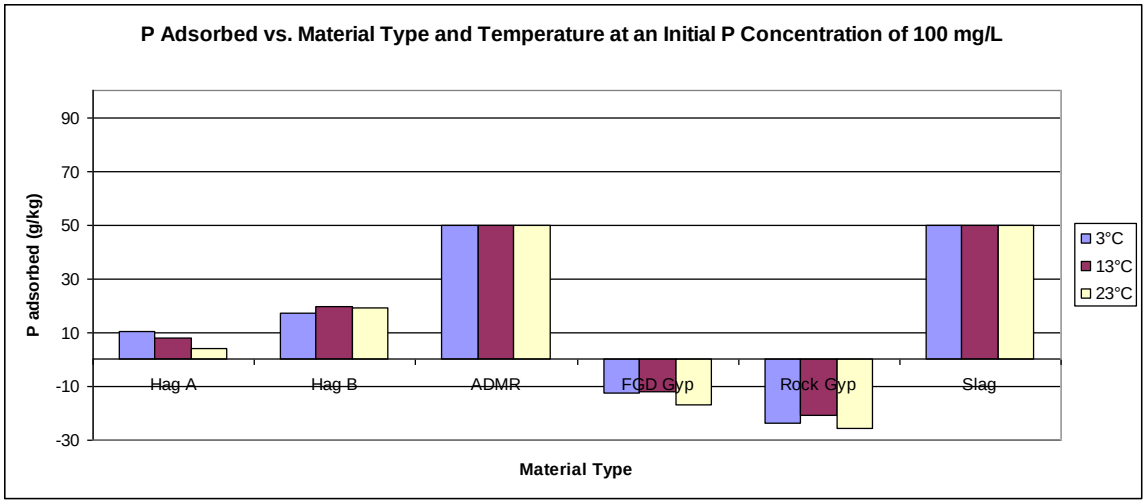
Appendix B: Isotherm data for each level of initial P as a function of temperature.





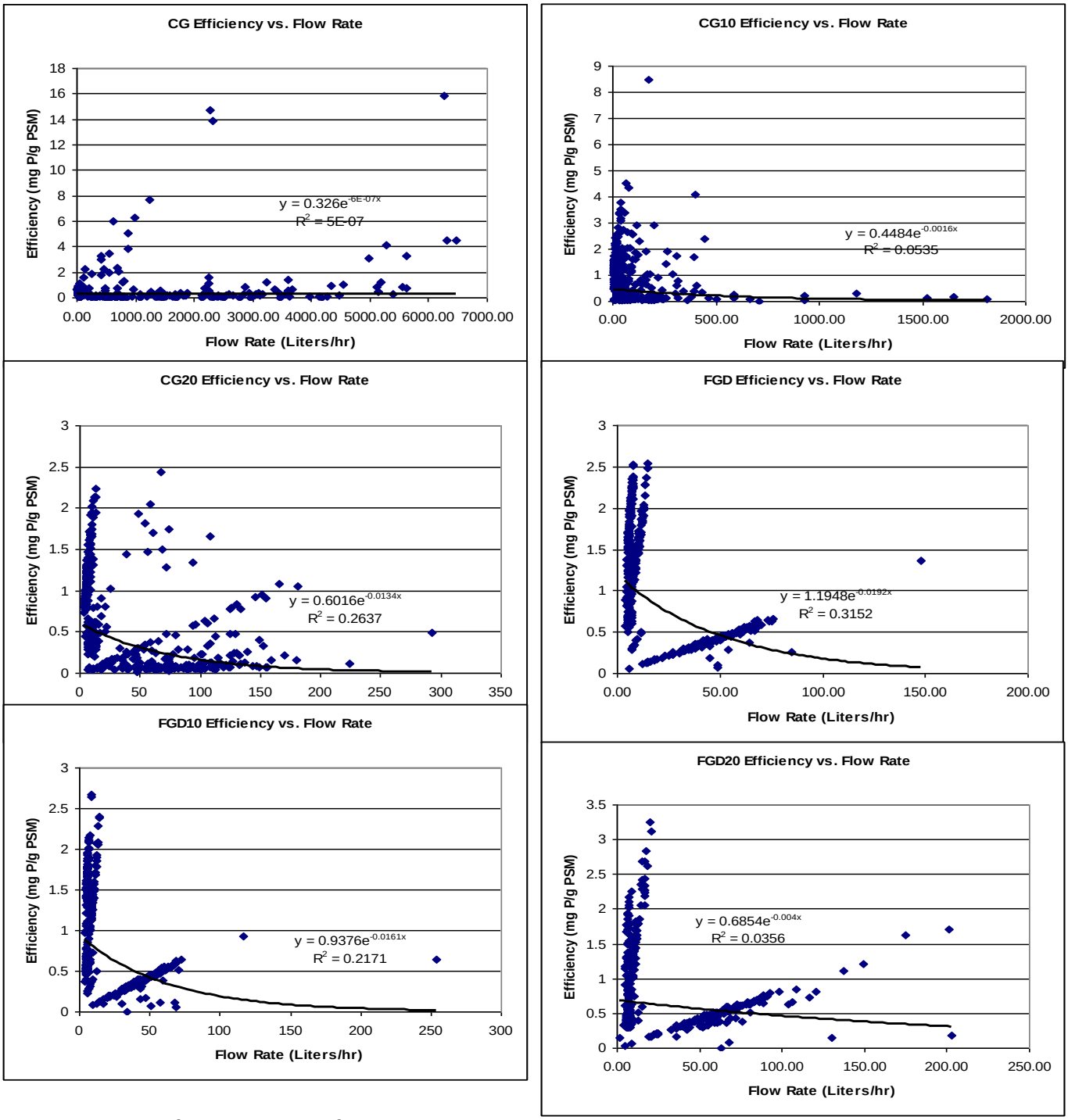


Figures 46a-c: Isotherm study data showing the P sorption of Hag A (Hagerstown A soil horizon), Hag B (Hagerstown B soil horizon), ADMR (Acid mind residuals), FGD gyp (flue-gas derived gypsum), rock gypsum, and steel slag for each temperature level at a given initial concentration of P in solution.

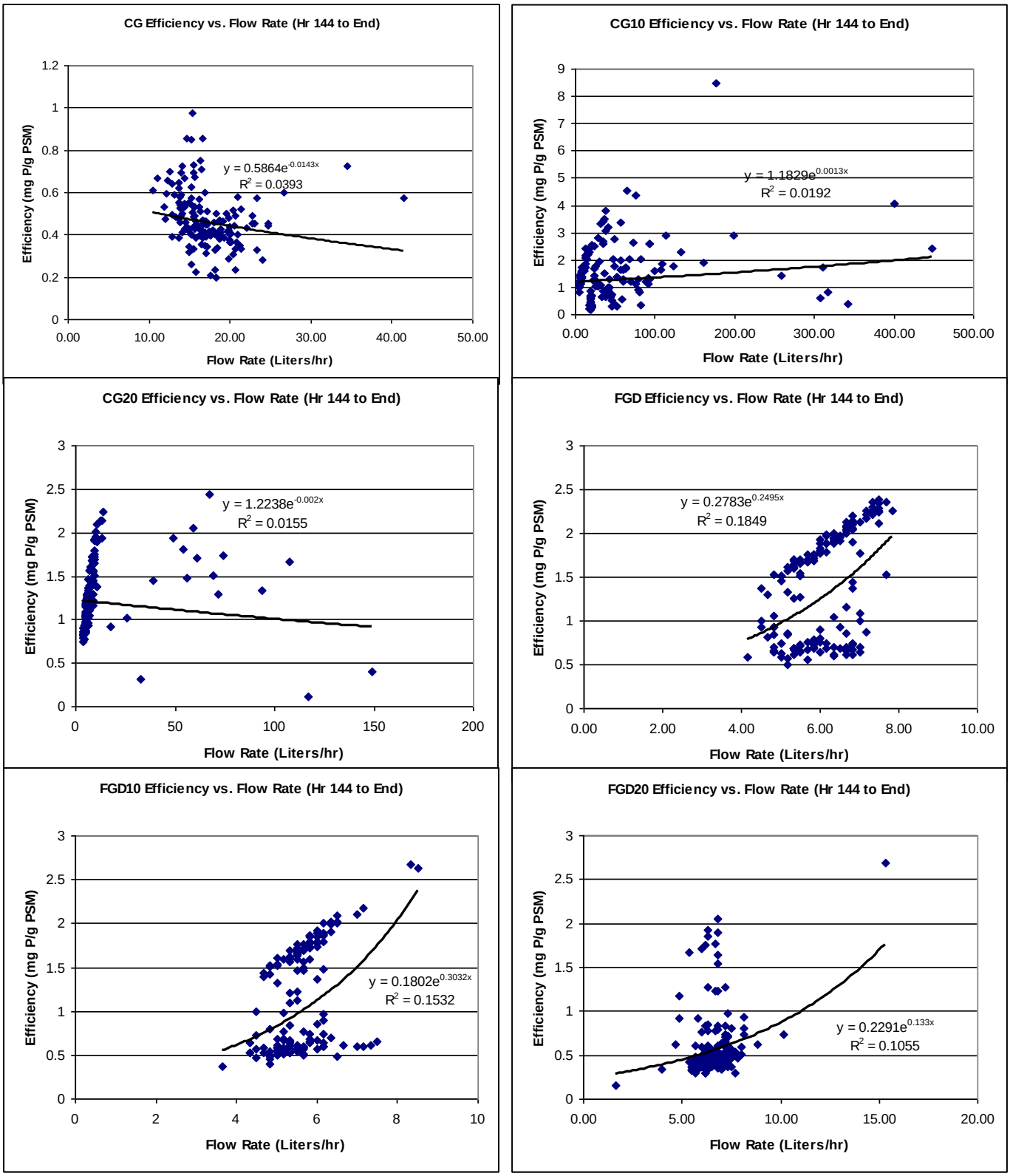


Figures 46d: Isotherm study data showing the P sorption of Hag A (Hagerstown A soil horizon), Hag B (Hagerstown B soil horizon), ADMR (Acid mind residuals), FGD gyp (flue-gas derived gypsum), rock gypsum, and steel slag for each temperature level at an initial concentration of 100 mg /liter.

Appendix C: Efficiency plotted against flow rate

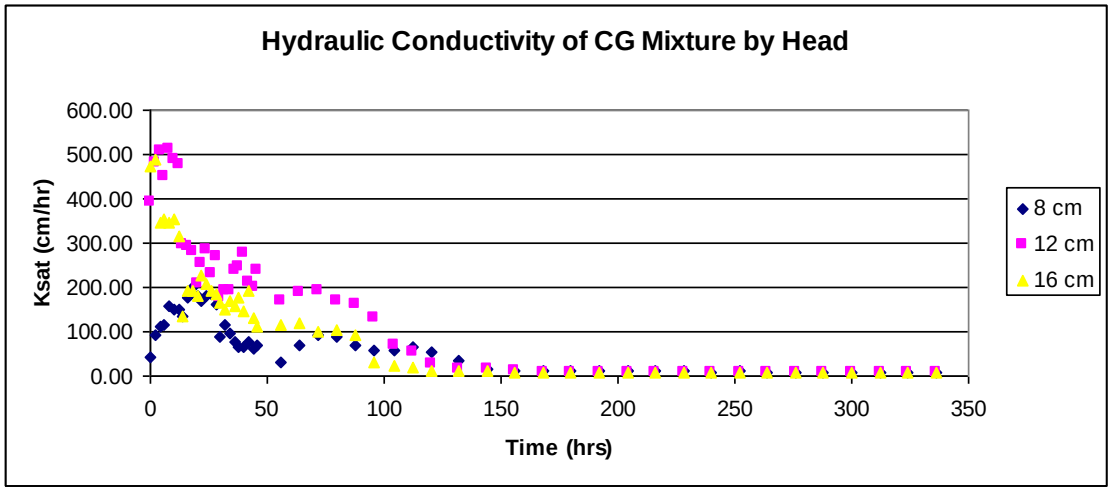


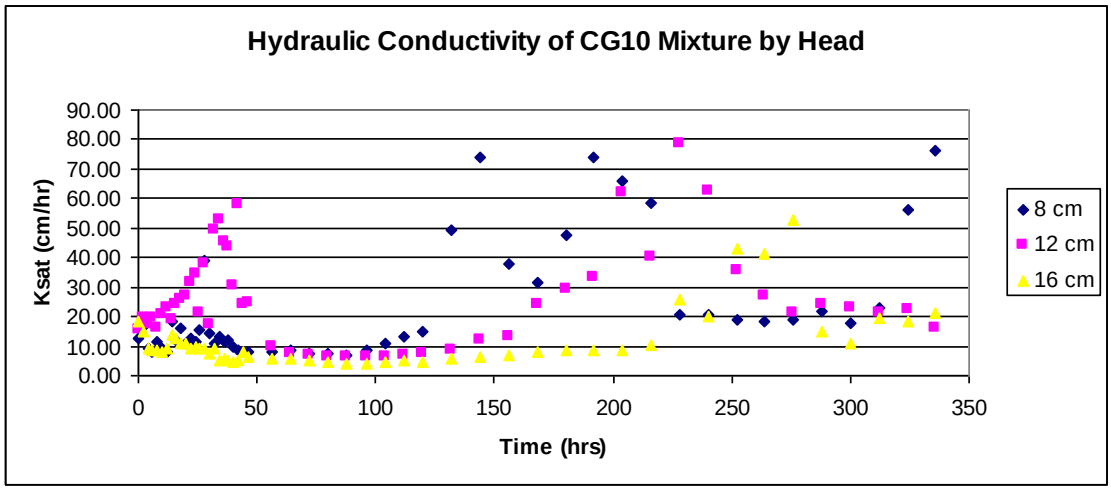
Figures 47a-f: Milligrams P flowing through columns retained by PSM divided by the grams CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against flow rate.

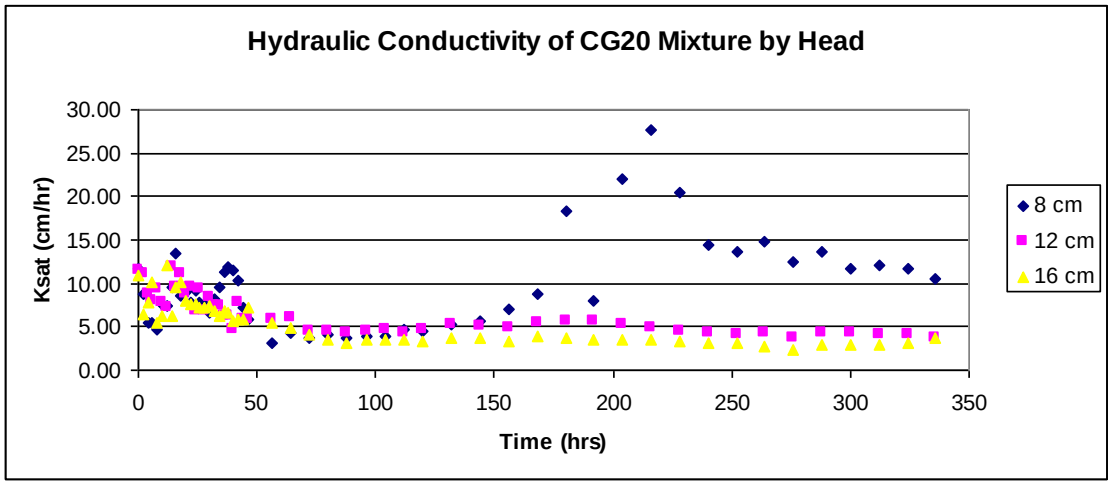


Figures 48a-f: Milligrams P flowing through columns retained by PSM divided by the grams CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) plotted against flow rate during the latter part of the study

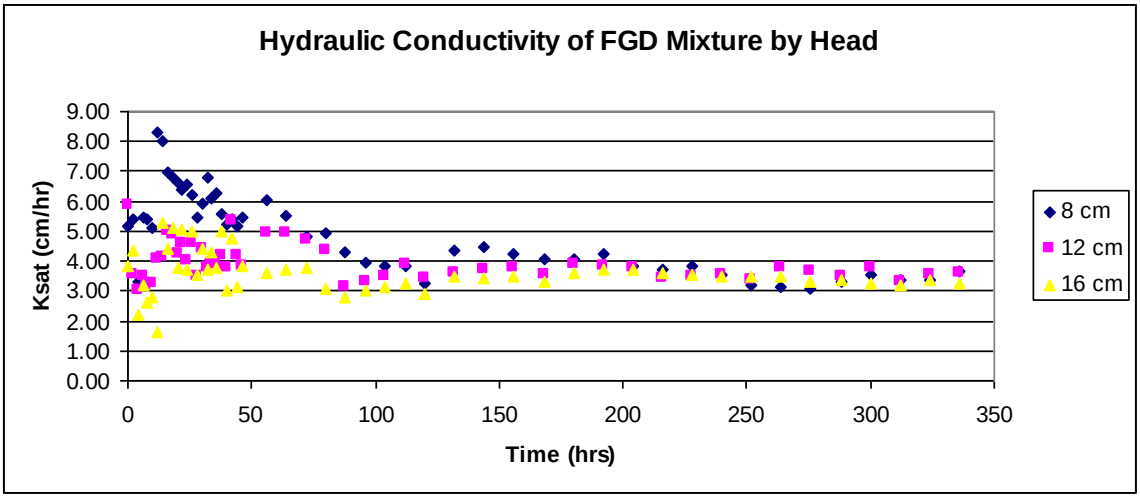
Appendix D: Hydraulic conductivity of each mixture as a function of hydraulic head.

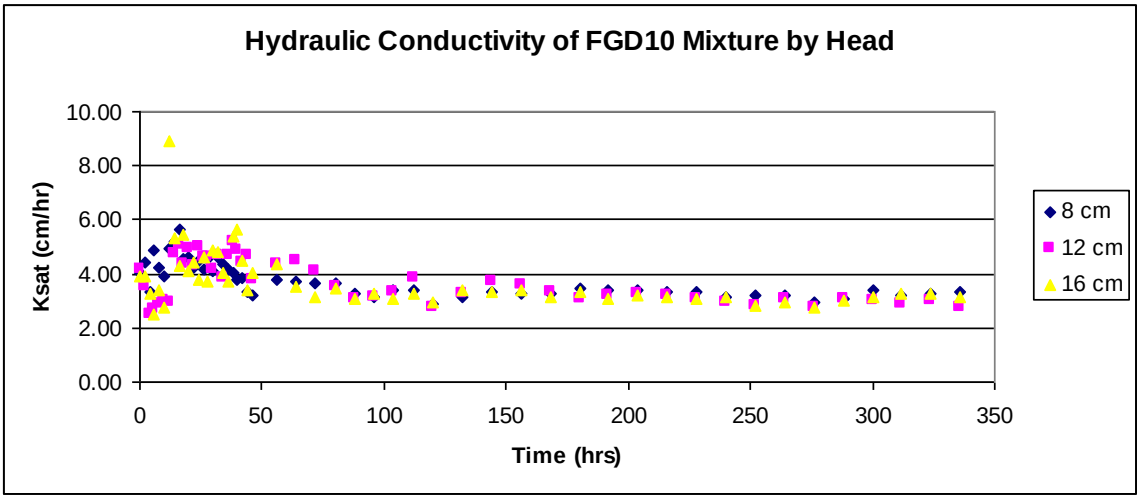


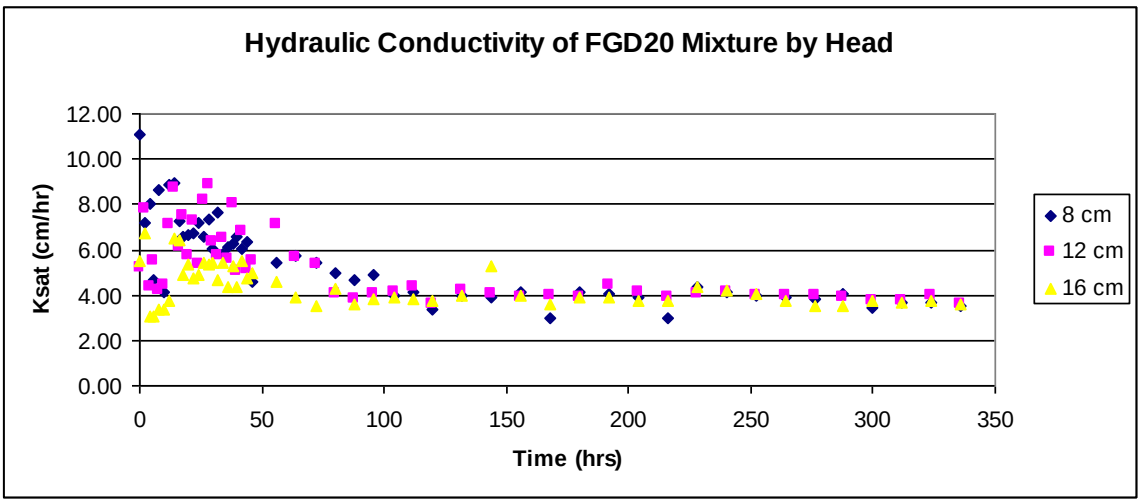




Figures 49a,b,c: Hydraulic Conductivity (K_{sat}) of the CG (coarse gypsum), CG10 (gypsum + 10% sand), and CG20 (gypsum + 20% sand) mixtures by pressure head

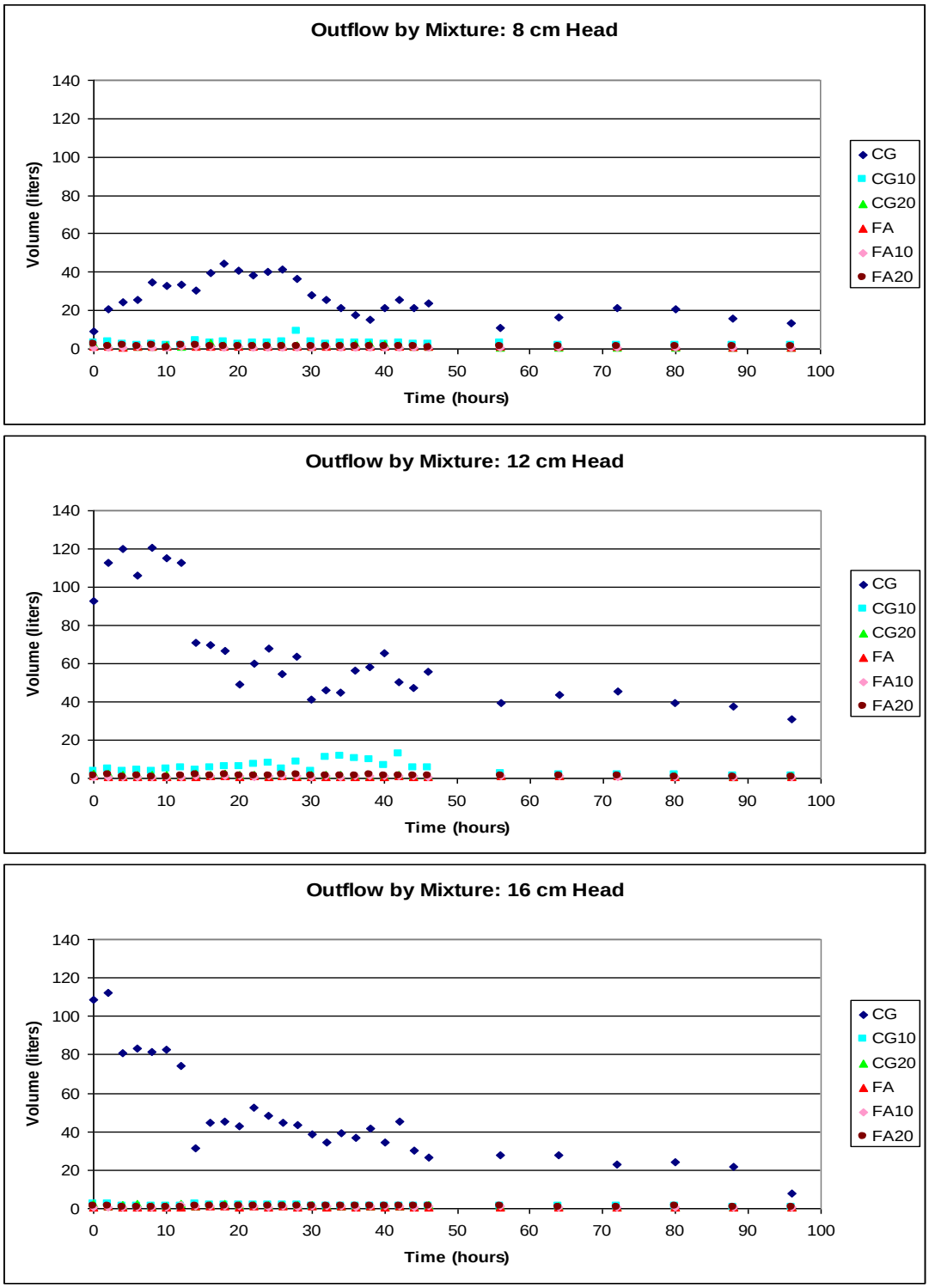






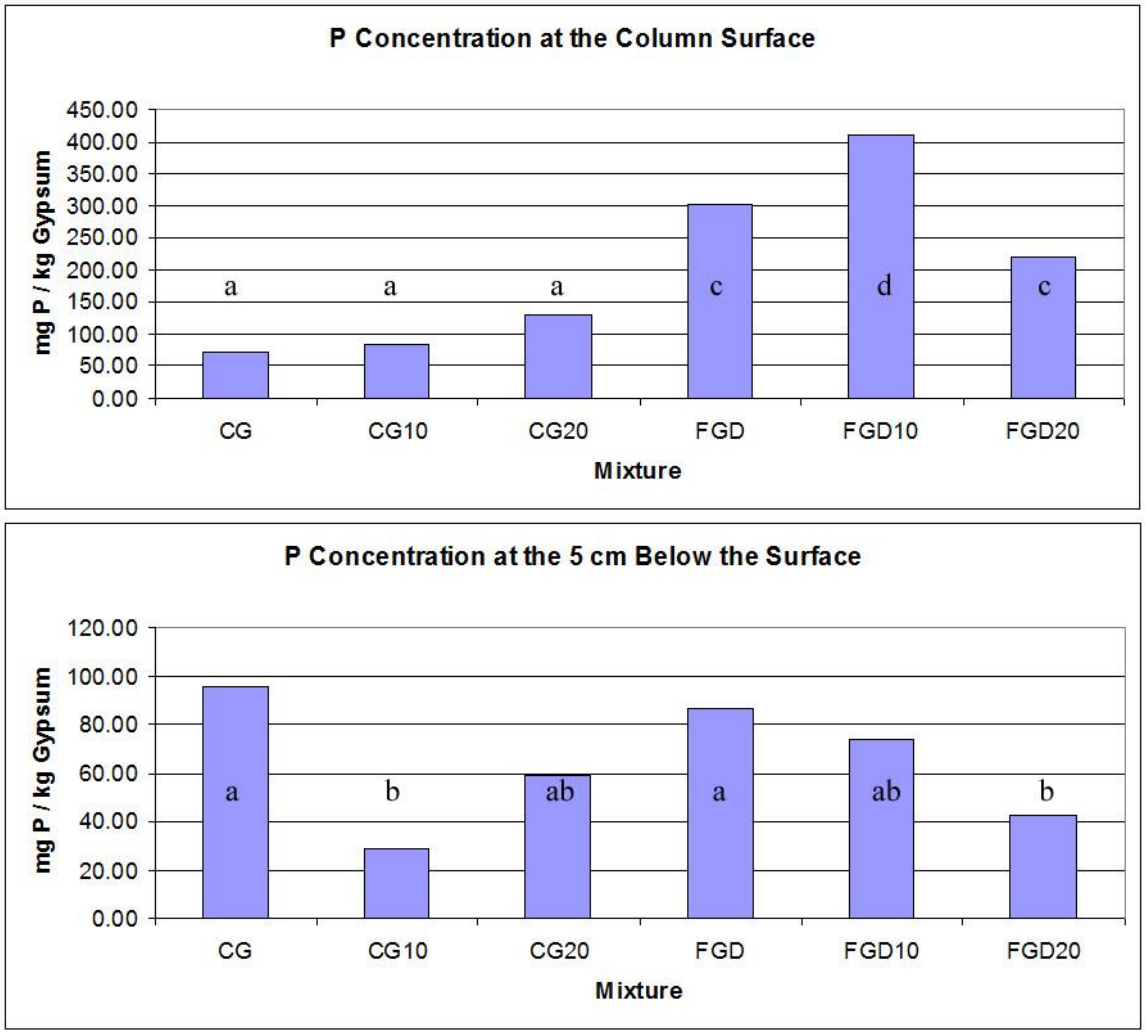
Figures 49e,d,f: Hydraulic Conductivity (K_{sat}) of the FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) mixtures by pressure head.

Appendix E: Column study outflow data as a function of hydraulic head.

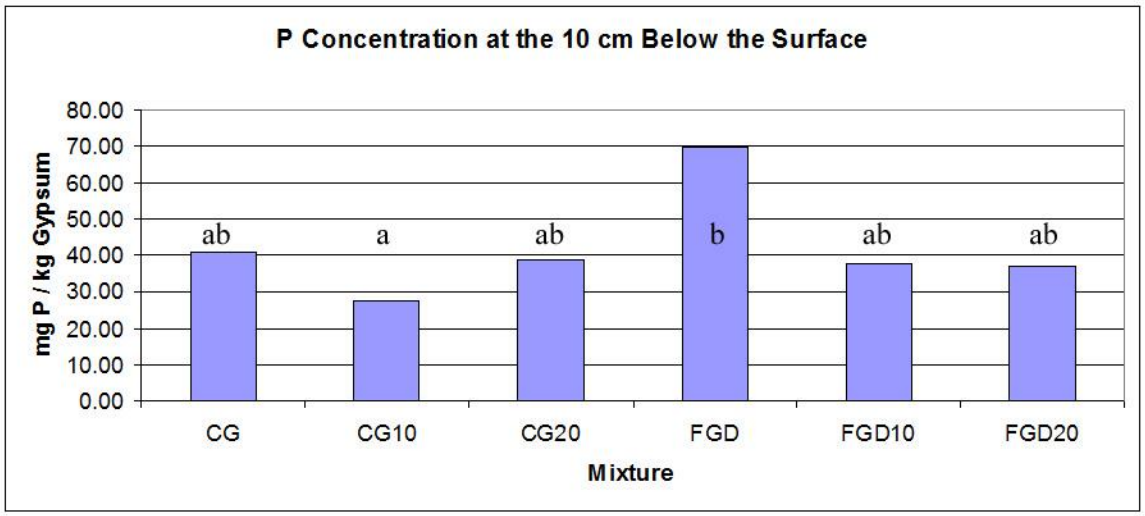


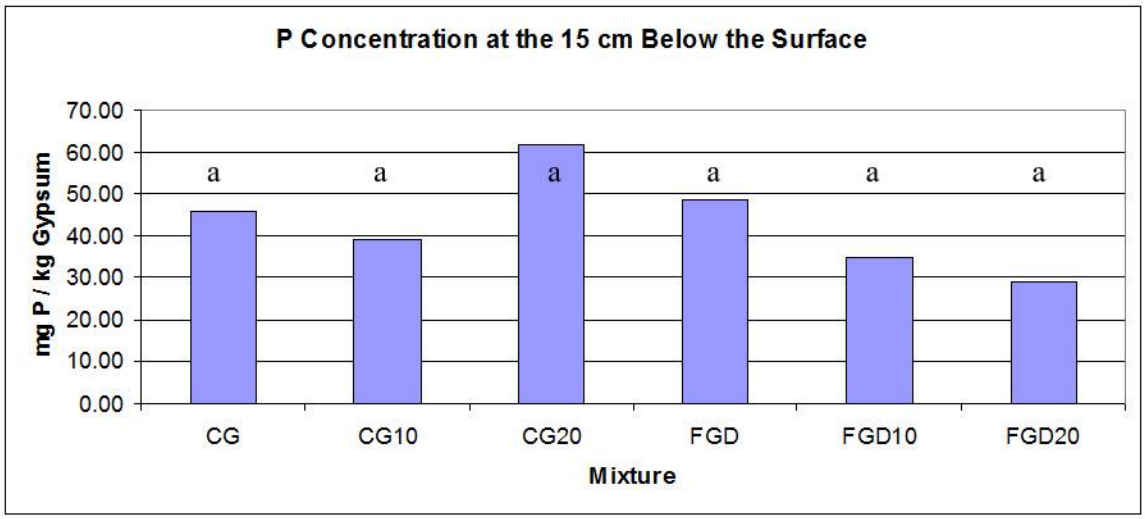
Figures 50a,b,c: Outflow data for CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand) separated by pressure head.

Appendix F: Location of P within Columns



Figures 51a,b: Sorbed phosphorus concentration found at the surface (within the top 1cm of the column) and at a depth of 5 cm by mixture: CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand).





Figures 51c,d: Sorbed phosphorus concentration found at the depths of 10 cm and 15cm by mixture: CG (coarse gypsum), CG10 (gypsum + 10% sand), CG20 (gypsum + 20% sand), FGD (flue gas derived gypsum), FGD10 (gypsum + 10% sand), and FGD20 (gypsum + 20% sand).

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